Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Iodine-Promoted Meyer-Schuster Rearrangement for the Synthesis of α-Iodo Unsaturated Ketones

Hai-Tao Zhu,*[a] Ming-Jin Fan,[a] De-Suo Yang,*[a] Xiao-Ling Wang,[a] Sen Ke,[a] Chao-Yang Zhang,[a] and Zheng-Hui Guan*[b]

[a] Shannxi Key Laboratory of Phytochemistry, Baoji University of Arts and Sciences, Baoji 721013, China. E-mail: 1888@bjwlxy.edu.cn;

[b] Key Laboratory of Synthesis and Natural Functional Molecule Chemistry of Ministry of Education, Department of Chemistry & Materials Science, Northwest University, Xi'an 710127, China. E-mail: guanzhh@nwu.edu.cn.

Table of Contents

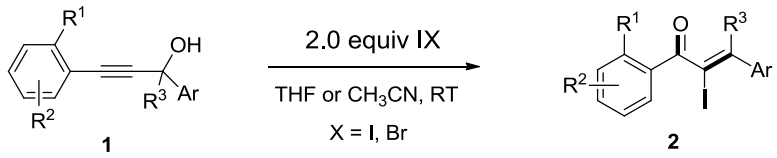
General Remarks

Column chromatography was carried out on silica gel (200-300 meshes). Conversion was monitored by thin layer chromatography (TLC). ^{1}H NMR spectra were recorded on 400 MHz in chloroform-d and ^{13}C NMR spectra were recorded on 100 MHz in in chloroform-d solution. IR spectra were recorded on a FT-IR spectrometer and only major peaks are reported in cm^{-1}. All products were further characterized by high resolution mass spectra (HRMS); copies of their ^{1}H NMR and ^{13}C NMR spectra are provided in the Supporting Information. Room temperature is 18–20℃ . Dry THF were distilled over CaH_2, and other commercial solvents were used without further purification.

Synthetic Procedures and Spectral Data

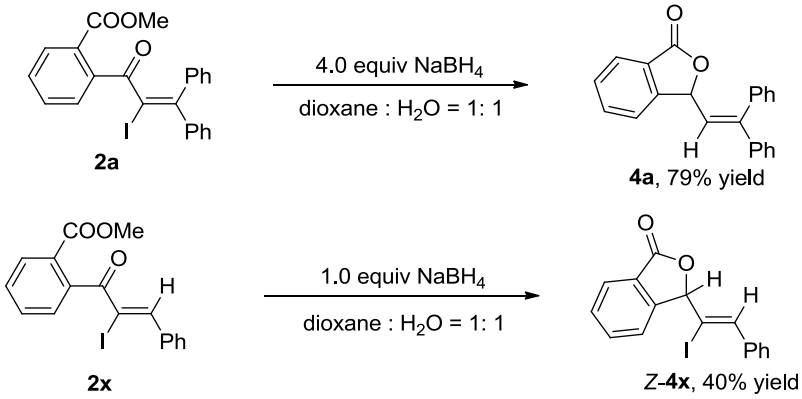
All starting materials were prepared according to previously reported procedures.[S1]

Synthesis of α-iodo unsaturated ketones:



To a solution of propargyl alcohol derivatives **1** (0.20 mmol) in THF or CH_3CN (4.0 mL) was added I_2 or IBr (2.0 equiv, 0.4 mmol) at room temperature. When the reaction was completed, the reaction mixture was quenched by addition of saturated aqueous sodium thiosulfate and extracted with ethyl acetate (3 x 15 mL), washed with water, saturated brine, dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford corresponding α-iodo unsaturated ketenes **2**.

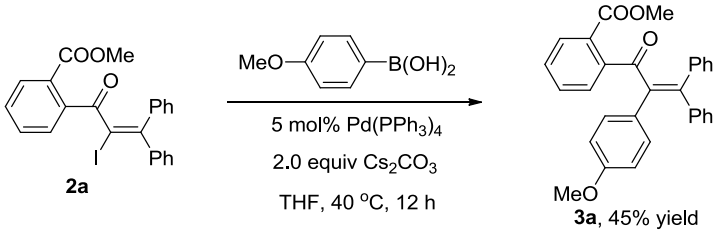
General procedure for reduction of α-iodo unsaturated ketones 2a and 2x:[S2]



To a stirred solution of **2a** or **2x** (0.5 mmol) in dioxane : H_2O (2 mL : 2 mL), was

added $NaBH_4$ (4.0 equiv or 1.0 equiv) in batches at ice-bath. After stirring for 0.5 h, the reaction was carried out at room temperature. When the reaction was considered to be complete as determined by TLC analysis, the reaction mixture was quenched by water and extracted with ethyl acetate (3 x 15 mL), washed with water, saturated brine, dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford 3-(2,2-diphenylvinyl)isobenzofuran-1-(3*H*)-one **4a** and (*Z*)-3-(1-iodo-2-phenylvinyl)isobenzofuran-1-(3*H*)-one **4x** in 79% and 40% yield, respectively.

General procedure for Suzuki coupling of α-iodo unsaturated ketones 2a:[S3]



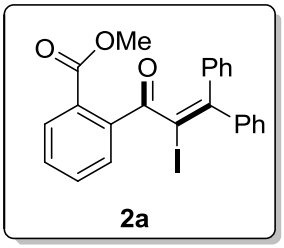
To a solution of **2a** (234 mg, 0.50 mmol) in anhydrous THF (6 mL) was added (4-methoxyphenyl)boronic acid (91.2 mg, 1.2 equiv), Cs_2CO_3 (326 mg, 2.0 equiv), $Pd(PPh_3)_4$ (29 mg, 0.05 equiv). The reaction vial was flushed with Ar and the reaction mixture was stirred for 12 h at 40°C. When the reaction was considered to be complete as determined by TLC analysis, the mixture was quenched by water (5 mL) and extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with water, brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by flash column chromatography to give **3a** in 45% yield.

Reference:

S1 a) H.-T. Zhu, K.-G. Ji, F. Yang, L.-J. Wang, Sh.-Ch. Zhao, A. Shaukat, X.-Y. Liu and Y.-M. Liang, *Org. Lett.*, 2011, **13**, 684; b) H.-T. Zhu, X. Dong, L.-J. Wang, M.-J. Zhong, X.-Y. Liu and Y.-M. Liang, *Chem.Commun.*, 2012, **48**, 10748.

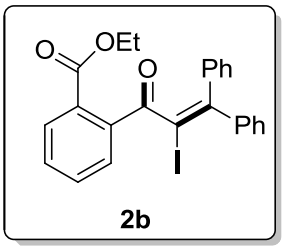
S2. a) D. Zhang and Ch. Yuan, *Eur. J. Org. Chem.*, 2007, 3916; b) A. K. Verma, S. P. Shukla, J. Singh and V. Rustagi, *J. Org. Chem.*, 2011, **76**, 5670.

S3. S. Puri, N. Thirupathi and M. S. Reddy, *Org. Lett.*, 2014, **16**, 5246-5249.



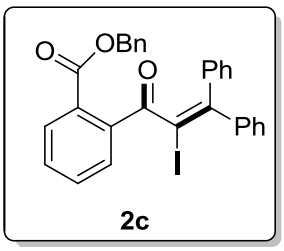
2a

Methyl-2-(2-iodo-3,3-diphenylacryloyl)benzoate **2a** ^{1}H NMR (400M Hz, $CDCl_3$) δ ppm 7.33 (d, *J* = 7.6 Hz, 2H), 7.32-7.26 (m, 3H), 7.19-7.12 (m, 4H), 6.95-6.91 (m, 5H), 3.90 (s, 3H). ^{13}C NMR (100M Hz,$CDCl_3$) δ ppm 193.3, 168.5, 158.6, 144.8, 139.7, 136.7, 132.1, 131.0, 130.4, 130.1, 129.7, 128.8, 128.7, 128.6, 128.2, 127.9, 101.3, 53.0. IR (neat, cm^{-1}): 2921, 1734, 1654, 1234, 1097, 763. HRMS (ESI) Calcd for $C_{23}H_{17}INaO_3$: M+Na = 491.0115. Found: 491.0121.



2b

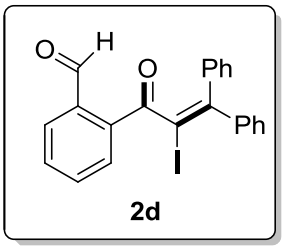
Ethyl-2-(2-iodo-3,3-diphenylacryloyl)benzoate 2b ^{1}H NMR (400M Hz, $CDCl_3$) δ ppm 7.39 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.31-7.28 (m, 3H), 7.24-7.13 (m, 4H), 6.97-6.90 (m, 5H), 4.38 (q, *J* = 7.6 Hz, 2H), 1.33 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100M Hz,$CDCl_3$) δ ppm 193.0, 168.1, 158.2, 144.8, 139.6, 136.3, 132.9, 131.1, 130.1, 129.9, 129.7, 128.8, 128.7, 128.6, 128.5, 128.2, 128.0, 101.0, 61.9, 14.1. IR (neat, cm^{-1}): 2922, 1725, 1663, 1258, 1096, 769. HRMS (ESI) Calcd for $C_{24}H_{19}INaO_3$: M+Na = 505.0271. Found: 505.0281.



2c

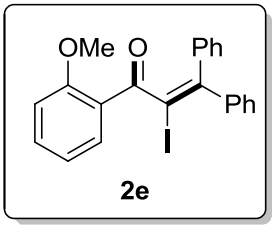
Benzyl-2-(2-iodo-3,3-diphenylacryloyl)benzoate 2c ^{1}H NMR (400M Hz, $CDCl_3$) δ ppm 7.43-7.37(m, 4H), 7.33-7.25(m, 6H), 7.21-7.13 (m, 4H), 6.89 (dd, *J* = 11.2, 7.6 Hz, 3H), 6.79 (t, *J* = 7.6 Hz, 2H), 5.35 (s, 2H). ^{13}C NMR (100M Hz,$CDCl_3$) δ ppm

193.0, 168.0, 158.2, 144.8, 139.6, 136.3, 135.5, 132.6, 131.2, 130.3, 129.9, 129.7, 129.0, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 100.7, 67.8. IR (neat, cm^{-1}): 2972, 1725, 1649, 1249, 1014, 754. HRMS (ESI) Calcd for $C_{29}H_{21}INaO_3$: M+Na = 567.0428. Found: 567.0441.



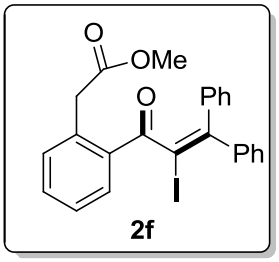
2d

2-(2-iodo-3,3-diphenylacryloyl)benzaldehyde 2d ^{1}H NMR (400M Hz, $CDCl_3$) δ ppm 10.17 (s,1H), 7.76-7.69 (m, 2H), 7.46-7.26 (m, 7H), 7.08-6.98 (m, 5H). ^{13}C NMR (100M Hz,$CDCl_3$) δ ppm 194.1, 191.3, 157.6, 143.2, 139.9, 138.9, 136.2, 132.3, 132.0, 129.6, 129.3, 129.1, 129.0, 128.9, 128.4, 128.3, 128.1, 98.3. IR (neat, cm^{-1}): 1689, 1663, 1589, 1234, 1192, 767. HRMS (ESI) Calcd for $C_{22}H_{15}INaO_2$: M+Na = 461.0009. Found: 461.0014.



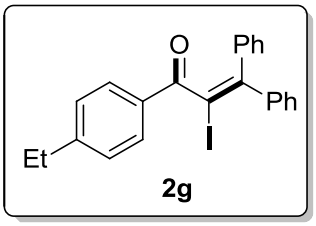
2e

2-Iodo-1-(2-methoxyphenyl)-3,3-diphenylprop-2-en-1-one 2e ^{1}H NMR (400M Hz, $CDCl_3$) δ ppm 7.56 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.43-7.39 (m, 2H), 7.36-7.31 (m, 4H), 7.07 (s, 5H), 6.86-6.80 (m, 2H), 3.93 (s, 3H).^{13}C NMR (100M Hz, $CDCl_3$) δ ppm 193.0, 158.2, 151.4, 144.2, 139.9, 133.9, 131.5, 129.2, 128.9, 128.2, 128.1, 128.0, 127.8, 125.9, 120.3, 111.3, 101.3, 55.6. IR (neat, cm^{-1}): 2849, 1649, 1483, 1289, 1013, 753. HRMS (ESI) Calcd for $C_{22}H_{17}INaO_2$: M+Na = 463.0165. Found: 463.0175.



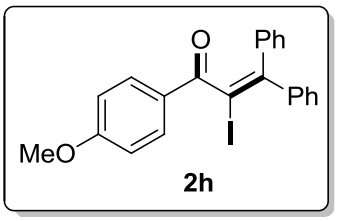
2f

Methyl-2-(2-(2-iodo-3,3-diphenylacryloyl)phenyl)acetate 2f ^{1}H NMR (400M Hz, $CDCl_3$) δ ppm 7.90 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.43-7.33 (m, 6H), 7.25-7.23 (m, 1H), 7.12 (d, J = 7.6 Hz, 1H),7.07-7.01 (m, 5H), 3.71 (s, 2H), 3.09 (s, 3H) .^{13}C NMR (100M Hz, $CDCl_3$) δ ppm 194.5, 171.4, 153.9, 143.5, 139.5, 135.9, 133.9, 132.6, 132.5, 131.2, 129.1, 128.9, 128.5, 128.4, 128.2, 128.0, 126.9, 98.3, 51.9, 40.1. IR (neat, cm^{-1}): 2943, 1718, 1658, 1230, 1086, 760. HRMS (ESI) Calcd for $C_{24}H_{19}INaO_3$: M+Na = 505.0271. Found: 505.0279.



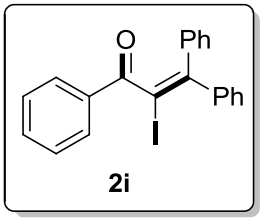
2g

1-(4-ethylphenyl)-2-iodo-3,3-diphenylprop-2-en-1-one 2g ^{1}H NMR (400M Hz, $CDCl_3$) δ ppm 7.77 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.39-7.28 (m, 4H), 7.10-7.05 (m, 2H), 7.04-6.99 (m, 4H), 2.56 (q, *J* = 8.0 Hz, 2H), 1.13(t, *J* = 8.0 Hz, 3H).^{13}C NMR (100M Hz, $CDCl_3$) δ ppm 193.2, 152.0, 150.4, 143.8, 139.2, 132.4, 130.1, 130.0, 129.4, 129.1, 128.3, 128.2, 128.1, 128.0, 96.3, 28.9, 14.9. IR (neat, cm^{-1}): 2931, 1653, 1441, 1239, 1073, 755. HRMS (ESI) Calcd for $C_{23}H_{19}INaO$: M+Na = 461.0373. Found: 461.0379.



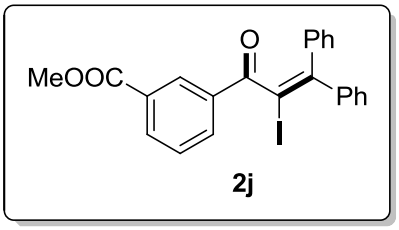
2h

2-iodo-1-(4-methoxyphenyl)-3,3-diphenylprop-2-en-1-one 2h. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.92 (d, *J* = 8.8 Hz, 2H), 7.45-7.36(m, 5H), 7.15-7.08 (m, 5H), 6.84 (d, *J* = 9.2 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 192.2, 163.7, 151.7, 143.8, 139.2, 129.3, 129.1, 128.4, 128.3, 128.1, 126.5, 113.8, 96.3, 55.4. IR (neat, cm^{-1}): 2931, 1638, 1595, 1252, 1159, 850. HRMS (ESI) Calcd for $C_{22}H_{18}IO_2$: M+H = 441.0346. Found: 441.0342.



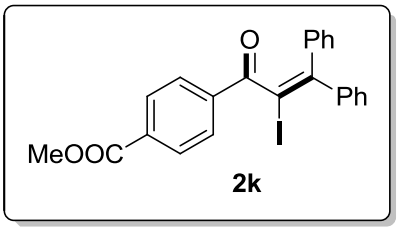
2i

2-iodo-1,3,3-triphenylprop-2-en-1-one 2i. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.92 (d, *J* =8.0 Hz, 2H), 7.46-7.39 (m, 6H), 7.35-7.32 (m, 2H), 7.12-7.06 (m, 5H).^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 193.6, 152.7, 143.6, 139.2, 133.9, 133.3, 129.7, 129.4, 129.1, 128.5, 128.4, 128.3, 128.1, 96.0. IR (neat, cm^{-1}): 1663, 1443, 1234, 1165, 932, 756. HRMS (ESI) Calcd for $C_{21}H_{15}INaO$: M+Na = 433.0060. Found: 433.0058.



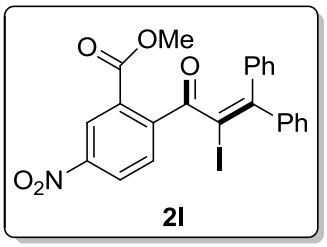
2j

Methyl-3-(2-iodo-3,3-diphenylacryloyl)benzoate 2j. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.54 (s, 1H), 8.09 (d, *J* = 7.6 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.45-7.38 (m, 6H), 7.09-7.04 (m, 5H), 3.93 (s, 3H). ^{13}CNMR (400 MHz, $CDCl_3$) δ ppm 192.8, 166.0, 153.9, 143.4, 139.2, 134.3, 133.9, 133.6, 130.9, 130.5, 129.4, 129.0, 128.7, 128.6, 128.4, 128.2, 95.4, 52.4. IR (neat, cm^{-1}): 2922, 1725, 1660, 1442, 1218, 761. HRMS (ESI) Calcd for $C_{23}H_{17}INaO_3$: M+Na = 491.0115. Found: 491.0124.



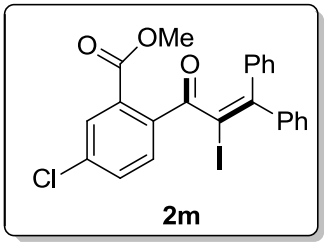
2k

Methyl-4-(2-iodo-3,3-diphenylacryloyl)benzoate 2k. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.97 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 8.8 Hz, 2H) 7.46-7.38 (m, 5H), 7.09-7.03 (m, 5H), 3.9 (s, 3H).^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 193.1, 166.0, 154.0, 143.3, 139.2, 137.6, 133.8, 129.6, 129.5, 129.4, 129.0, 128.8, 128.7, 128.4, 128.2, 95.4, 52.4. IR (neat, cm^{-1}): 2954, 1720, 1653, 1279, 1107, 790. HRMS (ESI) Calcd for $C_{23}H_{17}INaO_3$: M+Na = 491.0115. Found: 491.0123.



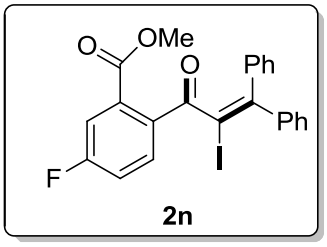
2l

Methyl-2-(2-iodo-3,3-diphenylacryloyl)-5-nitrobenzoate 2l ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.30 (d, *J* = 2.4 Hz, 1H), 7.99 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.41-7.37 (m, 4H), 7.25-7.23 (m, 2H), 7.09-7.05 (m, 1H), 6.99 (t, *J* = 7.6 Hz, 2H), 6.93-6.91 (m, 2H), 4.07 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 192.0, 165.7, 161.7, 147.8, 144.4, 143.4, 139.9, 132.1, 131.2, 129.9, 129.3, 129.2, 128.5, 128.3, 128.2, 125.1, 124.0, 102.0, 53.7. IR (neat, cm^{-1}): 2919, 1735, 1645, 1218, 997, 750. HRMS (ESI) Calcd for $C_{23}H_{17}INO_5$: M+H = 514.0146. Found: 514.0154.



2m

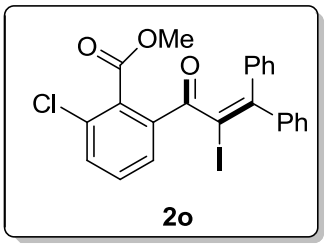
Methyl-5-chloro-2-(2-iodo-3,3-diphenylacryloyl)benzoate 2m. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.41-7.33 (m, 5H), 7.27 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.17 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.11-7.07 (m, 1H), 7.03 (t, *J* = 7.6 Hz, 2H), 6.97-6.95 (m, 2H), 3.99 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 192.4, 167.2, 159.0, 144.4, 139.7, 137.2, 135.0, 133.6, 131.4, 130.3, 129.7, 128.9, 128.8, 128.7, 128.6, 128.2, 128.1, 100.8, 53.3. IR (neat, cm^{-1}): 2924, 1733, 1658, 1232, 1089, 768. HRMS (ESI) Calcd for $C_{23}H_{16}ClINaO_3$: M+Na = 524.9725. Found: 524.9734.



2n

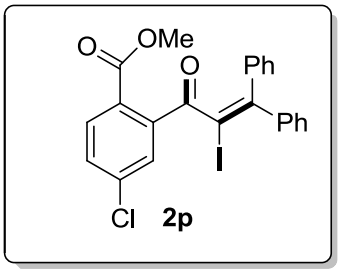
Methyl-5-fluoro-2-(2-iodo-3,3-diphenylacryloyl)benzoate 2n. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.48-7.41 (m, 1H), 7.39-7.33 (m, 3H), 7.28-7.27 (m, 2H), 7.13-7.09 (m,

1H), 7.08-7.01 (m, 3H), 6.99-6.91 (m, 2H), 6.88 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 192.1, 167.3 (d, *J* = 2 Hz), 164.7, 162.2, 158.6, 144.5, 139.6, 134.8 (d, *J* = 8 Hz), 132.8, 132.6 (d, *J* = 4 Hz), 129.7, 128.8 (d, *J* = 3 Hz), 128.6, 128.2 (d, *J* = 18 Hz), 117.1 (d, *J* = 22 Hz), 116.2 (d, *J* = 24 Hz), 100.6, 53.3. IR (neat, cm^{-1}): 2922, 1727, 1647, 1226, 1007, 752. HRMS (ESI) Calcd for $C_{23}H_{16}FINaO_3$: M+Na = 509.0020. Found: 509.0030.



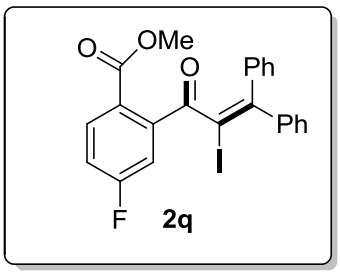
2o

Methyl-2-chloro-6-(2-iodo-3,3-diphenylacryloyl)benzoate 2o ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.63 (d, *J* = 7.6 Hz, 1H), 7.44-7.35 (m, 6H), 7.19 (t, *J* = 8.0, 1H), 7.10-7.04 (m, 5H), 4.00 (s, 3H).^{13}CNMR (400 MHz, $CDCl_3$) δ ppm 191.7, 166.8, 156.6, 143.7, 139.0, 133.9, 133.8, 133.6, 132.2, 129.7, 129.0, 128.9, 128.8, 128.5, 128.4, 128.3, 96.0, 53.0 . IR (neat, cm^{-1}): 2926, 1730, 1655, 1229, 1090, 764. HRMS (ESI) Calcd for $C_{23}H_{16}ClINaO_3$: M+Na = 524.9725. Found: 524.9731.

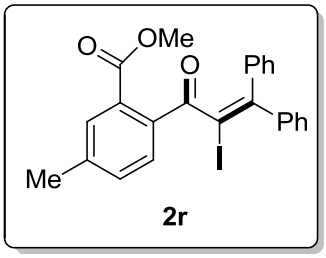


2p

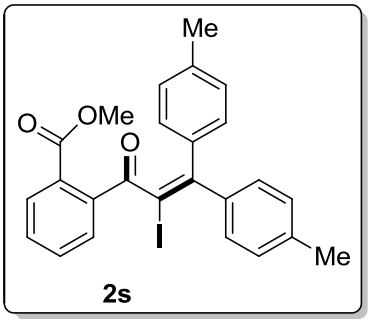
2p. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.41-7.35 (m, 4H), 7.24 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.16-7.11 (m, 2H), 7.10-7.07 (m, 1H), 7.02 (t, *J* = 7.6 Hz, 2H), 6.93-6.90 (m, 2H), 4.01 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 192.5, 167.1, 160.6, 144.7, 139.8, 139.6, 137.1, 130.5, 130.3, 129.7, 129.1, 129.0, 128.9, 128.5, 128.3, 128.0, 102.2, 53.4. IR (neat, cm^{-1}): 2923, 1737, 1657, 1235, 1092, 776. HRMS (ESI) Calcd for $C_{23}H_{16}ClINaO_3$: M+Na = 524.9725. Found: 524.9736.



Methyl-4-fluoro-2-(2-iodo-3,3-diphenylacryloyl)benzoate 2q. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.47 (dd, *J* = 8.4, 5.2 Hz, 1H), 7.40-7.32 (m, 3H), 7.24 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.09-7.07 (m, 2H), 6.93-6.86(m, 4H), 4.00(s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 192.4 (d, *J* = 2 Hz), 167.0, 163.2 (d, *J* = 252 Hz), 160.3, 144.7, 140.5 (d, *J* = 8 Hz), 139.8, 131.4 (d, *J* = 8 Hz), 129.7, 128.8 (d, *J* = 3 Hz), 128.5, 128.2, 128.0, 127.2 (d, *J* = 3 Hz), 117.3 (d, *J* = 22 Hz), 102.0, 53.3 (d, *J* = 3 Hz). IR (neat, cm^{-1}): 2919, 1724, 1643, 1221, 998, 750. HRMS (ESI) Calcd for $C_{23}H_{16}FINaO_3$: M+Na = 509.0020. Found: 509.0027.

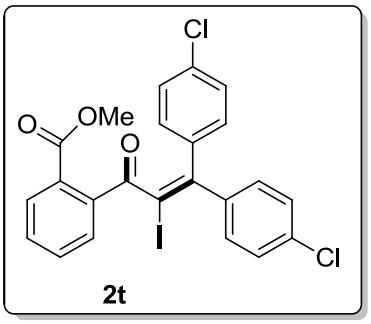


Methyl-2-(2-iodo-3,3-diphenylacryloyl)-5-methylbenzoate 2r ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.44-7.35 (m, 4H), 7.31-7.29 (m, 2H), 7.23 (s, 1H), 7.06-7.01 (m, 6H), 3.96 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 193.0, 169.0, 157.3, 144.6, 142.3, 139.5, 133.2, 132.9, 130.7, 130.4, 129.6, 129.5, 128.7, 128.6, 128.5, 128.3, 127.9, 100.4, 53.0, 21.2. IR (neat, cm^{-1}): 2948, 2923, 1738, 1660, 1219, 770. HRMS (ESI) Calcd for $C_{24}H_{19}INaO_3$: M+Na = 505.0271. Found: 505.0279.



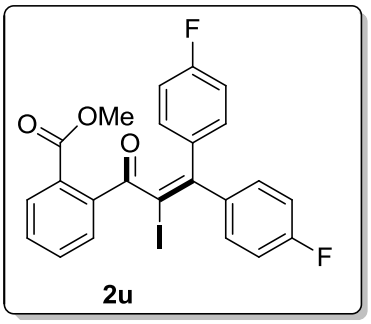
Methyl-2-(2-iodo-3,3-di-p-tolylacryloyl)benzoate 2s. ^{1}H NMR (400 MHz, $CDCl_3$) δ

ppm 7.44-7.41 (m, 2H), 7.28-7.23 (m, 2H), 7.21-7.18 (m, 4H), 6.85 (d, J = 8.0 Hz, 2H), 6.78 (d, J = 8.0 Hz, 2H), 3.98 (s, 3H), 2.38 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 193.5, 168.6, 159.1, 141.9, 138.8, 137.2, 136.9, 132.1, 130.7, 130.3, 130.2, 129.8, 128.8, 128.7, 128.6, 100.2, 53.0, 21.4, 21.1. IR (neat, cm^{-1}): 2941, 2922, 1735, 1652, 1245, 788. HRMS (ESI) Calcd for $C_{25}H_{21}INaO_3$: M+Na = 519.0428. Found: 519.0439.



2t

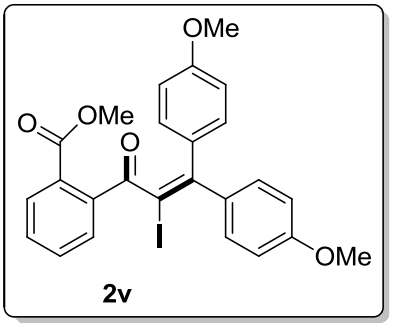
Methyl-2-(3,3-bis(4-chlorophenyl)-2-iodoacryloyl)benzoate 2t. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.48 (dd, J = 7.6, 0.8 Hz, 1H), 7.42 (dd, J = 7.6, 1.2 Hz, 1H), 7.39-7.27 (m, 4H), 7.23-7.20 (m, 2H), 6.99 (dd, J = 6.8, 2.0 Hz, 2H), 6.91 (dd, J = 6.8, 2.0 Hz, 2H), 3.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 193.0, 168.3, 155.8, 142.5, 137.6, 136.4, 135.0, 134.9, 132.3, 131.4, 130.9, 130.1, 130.2, 130.0, 129.0, 128.7, 128.3, 102.4, 53.1. IR (neat, cm^{-1}): 2919, 1735, 1657, 1228, 1086, 750. HRMS (ESI) Calcd for $C_{23}H_{15}Cl_2INaO_3$: M+Na = 558.9335. Found: 558.9332.



2u

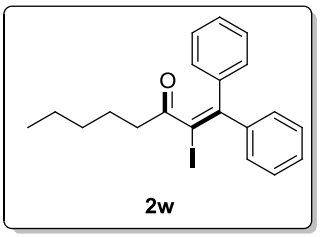
Methyl-2-(3,3-bis(4-fluorophenyl)-2-iodoacryloyl)benzoate 2u. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.47-7.41 (m, 2H), 7.34-7.25 (m, 4H), 7.11-7.07 (m, 2H), 6.98-6.94 (m, 2H), 6.72-6.68 (m, 2H), 3.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 193.2, 168.4, 162.7 (dd, J = 249, 6 Hz), 156.5, 140.3 (d, J = 3 Hz), 136.5, 135.6 (d, J = 4 Hz), 132.1, 131.7 (d, J = 9 Hz), 131.3, 130.8 (d, J = 9 Hz), 130.5, 129.9, 128.9, 115.2 (dd, J = 27, 22 Hz), 101.8, 53.1. IR (neat, cm^{-1}): 2917, 1731, 1652, 1223, 1079, 746.

HRMS (ESI) Calcd for $C_{23}H_{15}F_2INaO_3$: M+Na = 526.9926. Found: 526.9932.



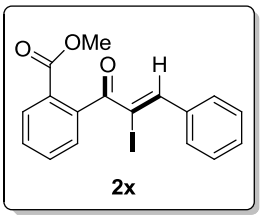
2v

Methyl-2-(2-iodo-3,3-bis(4-methoxyphenyl)acryloyl)benzoate 2v. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.43-7.38 (m, 2H), 7.27-7.21 (m, 4H), 6.91-6.87 (m, 4H), 6.50 (d, *J* = 8.4 Hz, 2H), 3.99 (s, 3H), 3.84 (s, 3H), 3.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 193.7, 168.6, 160.1, 160.0, 159.2, 137.4, 137.1, 133.1, 131.9, 130.9, 130.6, 130.3, 130.1, 128.7, 113.4, 110.3, 99.3, 55.2, 55.2, 53.1. IR (neat, cm^{-1}): 2926, 1734, 1661, 1241, 1103, 775. HRMS (ESI) Calcd for $C_{25}H_{22}IO_5$: M+H = 529.0506. Found: 529.0515.



2w

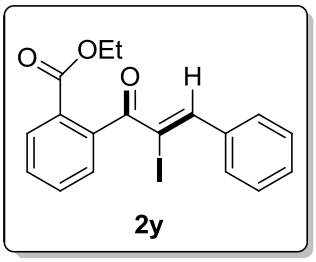
2-iodo-1,1-diphenyloct-1-en-3-one 2w. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.32-7.28 (m, 3H), 7.23-7.17 (m, 5H) , 7.06 (d, *J* = 7.6 Hz, 2H), 2.20 (t, *J* = 7.2 Hz, 2H), 1.41-1.34 (m, 2H), 1.12-1.04 (m, 2H), 1.03-0.97 (m, 2H), 0.73 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 203.9, 152.2, 143.7, 139.5, 129.4, 128.9, 128.8, 128.5, 128.4, 128.2, 100.1, 41.0, 31.1, 24.1, 22.2, 13.8. IR (neat, cm^{-1}): 2921, 1726, 1649, 1290, 1013, 755. HRMS (ESI) Calcd for $C_{20}H_{21}INaO$: M+Na = 427.0529. Found: 427.0540.



2x

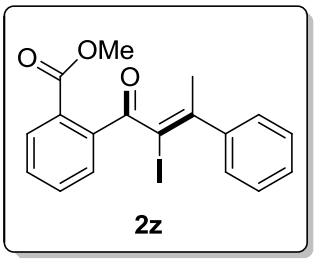
(Z)-methyl-2-(2-iodo-3-phenylacryloyl)benzoate 2x. ^{1}H NMR (400 MHz, $CDCl_3$) δ

ppm 7.96 (d, *J* = 7.6 Hz, 1H), 7.62-7.60 (m, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.40 (s, 1H), 7.32-7.29 (m, 4H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 192.9, 165.7, 150.3, 139.5, 135.0, 132.4, 130.3, 129.8, 129.5, 129.0, 128.2, 127.8, 108.3, 52.8. IR (neat, cm^{-1}): 2922, 1733, 1646, 1230, 1094, 758. HRMS (ESI) Calcd for $C_{17}H_{13}INaO_3$: M+Na = 414.9802. Found: 414.9810.



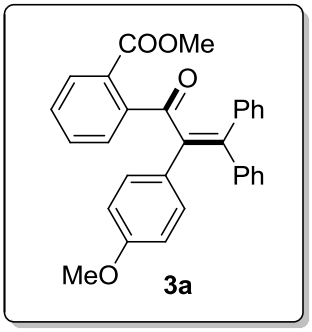
2y

(Z)-ethyl-2-(2-iodo-3-phenylacryloyl)benzoate 2y. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.98 (d, *J* = 8.0 Hz, 1H), 7.63-7.61 (m, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.45 (s, 1H), 7.31-7.29 (m, 4H), 4.20 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 192.8, 165.3, 150.8, 139.5, 135.1, 132.3, 130.4, 129.8, 129.6, 129.4, 128.2, 127.8, 108.6, 61.8, 14.1. IR (neat, cm^{-1}): 2924, 1735, 1645, 1224, 1090, 761. HRMS (ESI) Calcd for $C_{18}H_{15}INaO_3$: M+Na = 428.9958. Found: 428.9962.

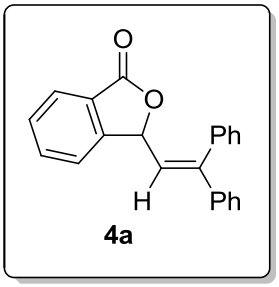


2z

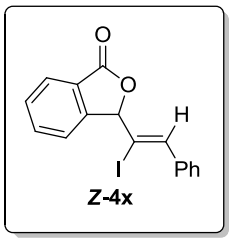
(Z)-methyl-2-(2-iodo-3-phenylbut-2-enoyl)benzoate 2z. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.40 (d, *J* = 6.8 Hz, 1H), 7.29 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.25-7.18 (m, 2H), 7.02 (s, 5H), 3.89 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 192.9, 168.4, 154.9, 140.1, 137.0, 131.9, 130.8, 130.3, 129.7, 128.8, 128.2, 128.0, 127.9, 102.0, 52.9, 32.9. IR (neat, cm^{-1}): 2943, 2921, 1732, 1651, 1242, 755. HRMS (ESI) Calcd for $C_{18}H_{15}INaO_3$: M+Na = 428.9958. Found: 428.9965.



Methyl-2-(2-(4-methoxyphenyl)-3,3-diphenylacryloyl)benzoate 3a ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.70 (d, *J* =7.6 Hz, 1H), 7.41(d, *J* = 6.8 Hz, 1H), 7.32-7.28 (m, 2H), 7.17 (d, *J* = 5.2 Hz,3H), 7.10-7.08 (m, 9H), 6.67 (d, *J* = 8.4 Hz, 2H), 3.89 (s, 3H), 3.72 (s, 3H).^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 198.2, 169.3, 158.6, 148.4, 141.9, 141.8, 139.2, 139.1, 133.0, 132.3, 131.9, 131.1, 130.9, 130.5, 130.4, 130.0, 128.6, 128.1, 128.0, 127.9, 127.7, 113.6, 55.1, 52.6 . IR (neat, cm^{-1}): 2970, 1728, 1654, 1489, 1240, 1165, 850, 754. HRMS (ESI) Calcd for $C_{30}H_{24}NaO_4$: M+Na = 471.1567. Found: 471.1568.



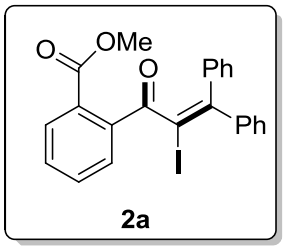
3-(2,2-diphenylvinyl)isobenzofuran-1(3*H*)-one 4a ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.83 (d, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.41-7.32 (m, 6H), 7.21-7.18 (m, 5H), 5.89 (d, *J* = 10.0 Hz, 1H), 5.81 (d, *J* = 10.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.5, 149.5, 149.4, 140.6, 138.1, 134.1, 129.9, 129.3, 128.6, 128.5, 128.3, 128.2, 127.8, 126.0, 125.7, 122.6, 122.5, 79.4. IR (neat, cm^{-1}): 1773, 1645, 1450, 1258, 1019, 754. HRMS (ESI) Calcd for $C_{22}H_{17}O_2$: M+H = 313.1223. Found: 313.1230.



Z-4x

(Z)-3-(1-iodo-2-phenylvinyl)isobenzofuran-1(3*H*)-one 4x ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.96 (d, *J* = 7.6 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.63-7.59 (m, 3H), 7.53 (s, 1H), 7.50 (d, *J* = 6.4 Hz, 1H), 7.39-7.35 (m, 3H), 5.87 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 169.6, 148.2, 139.5, 135.9, 134.4, 129.9, 129.0, 128.8, 128.2, 126.8, 125.6, 122.5, 102.3, 86.5. IR (neat, cm^{-1}): 1778, 1640, 1465, 1231, 1097, 760. HRMS (ESI) Calcd for $C_{16}H_{11}INaO_2$: M+Na = 384.9696. Found: 384.9699.

Crystallographic data of 2a



2a

Datablock:

Bond precision: C-C = 0.0045 A Wavelength=0.71073

Cell: a=26.291(14) b=8.781(5) c=18.363(10)
alpha=90 beta=111.863(4) gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	3934(4)	3935(4)
Space group	C 2/c	C2/c
Hall group	-C 2yc	?
Moiety formula	C23 H17 I O3	?
Sum formula	C23 H17 I O3	C23 H17 I O3
Mr	468.27	468.27
Dx,g cm-3	1.581	1.581
Z	8	8

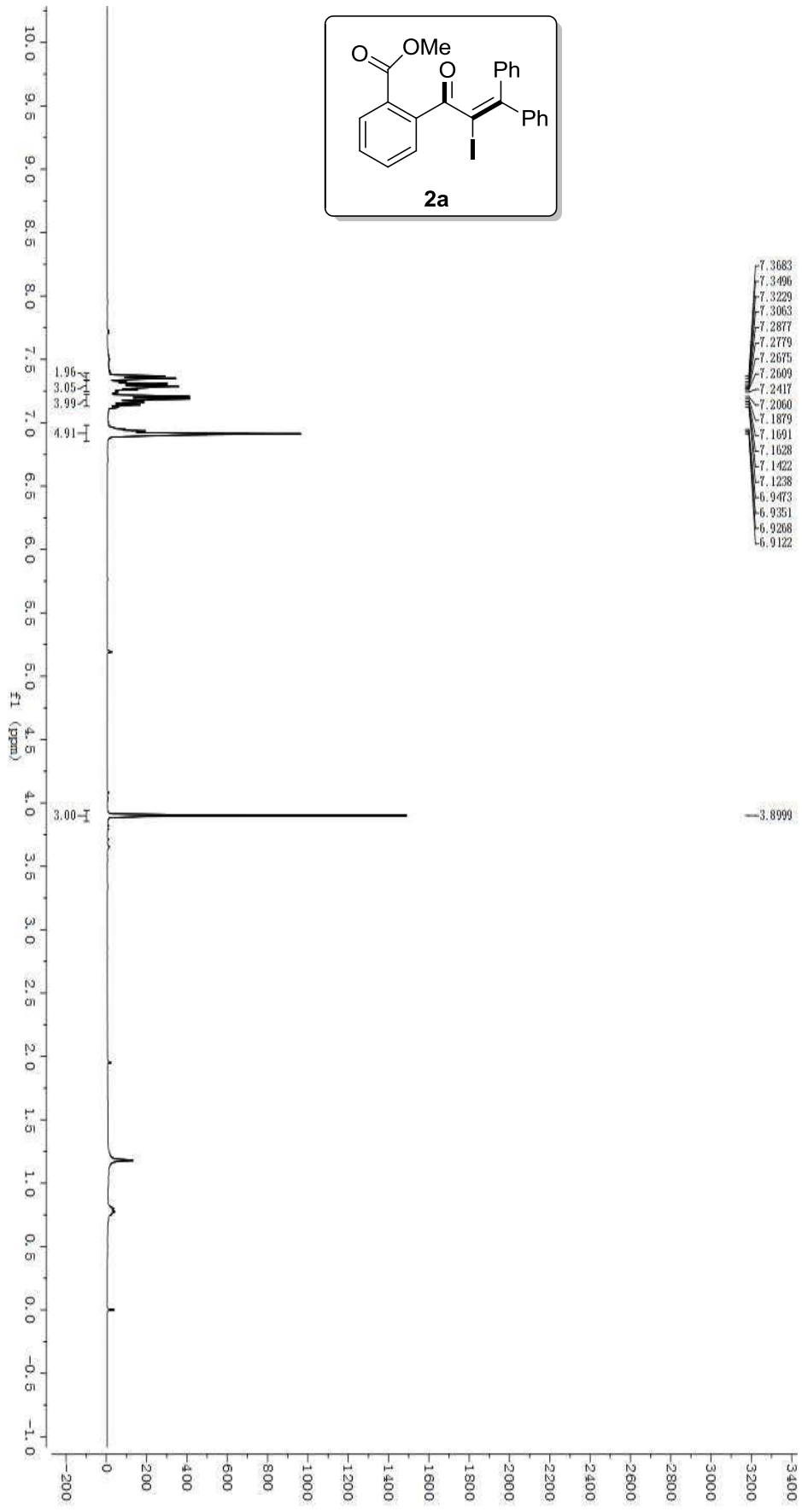
Mu (mm-1)	1.648	1.647
F000	1856.0	1856.0
F000'	1852.96	
h,k,lmax	31,10,22	31,10,22
Nref	3672	3666
Tmin,Tmax	0.692,0.877	0.703,0.879
Tmin'	0.678	

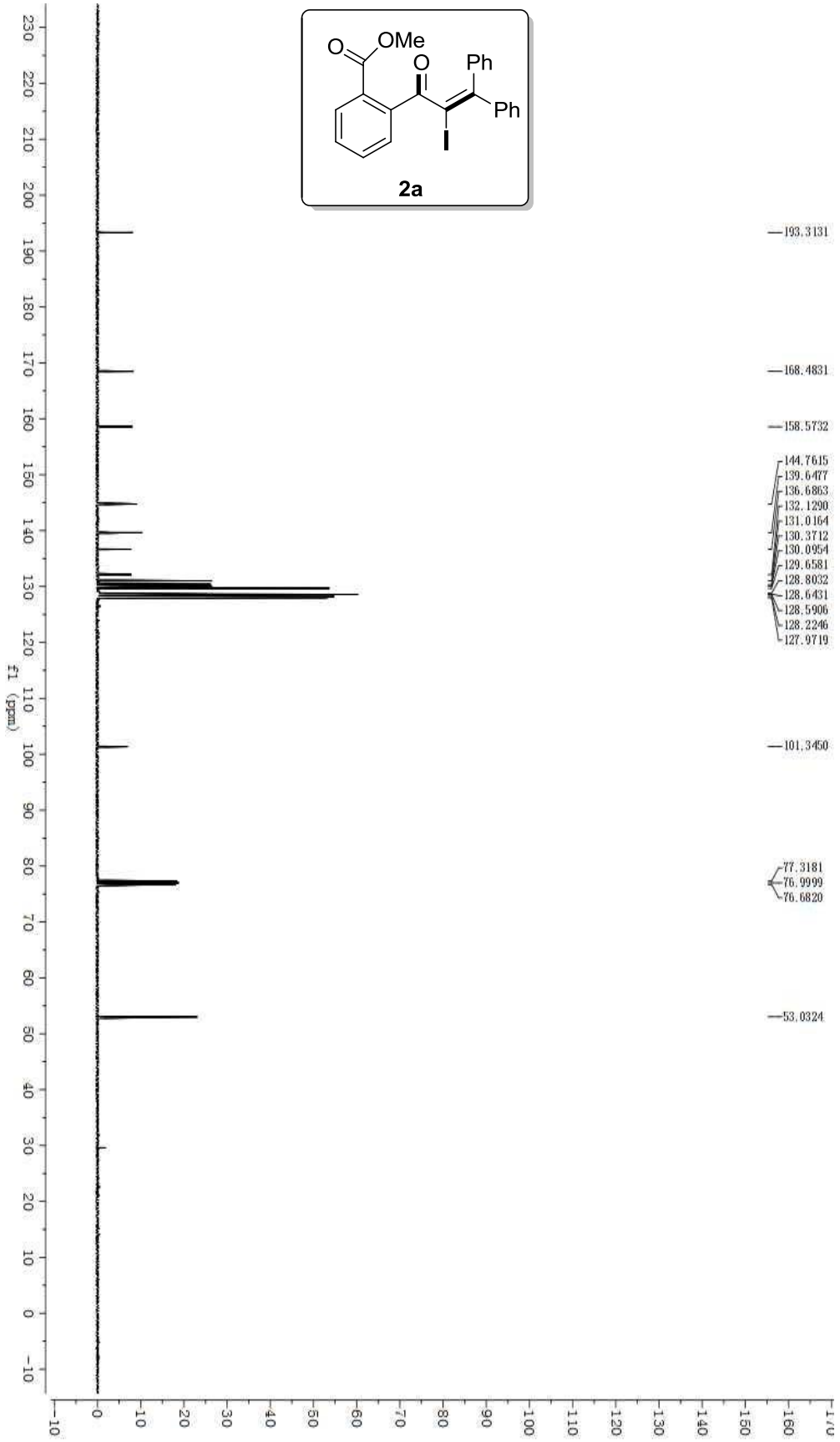
Correction method= MULTI-SCAN

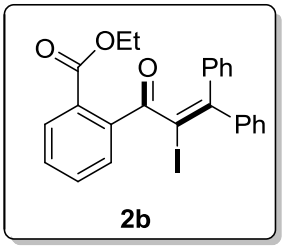
Data completeness= 0.998 Theta(max)= 25.500

R(reflections)= 0.0247(2987) wR2(reflections)= 0.0529(3666)

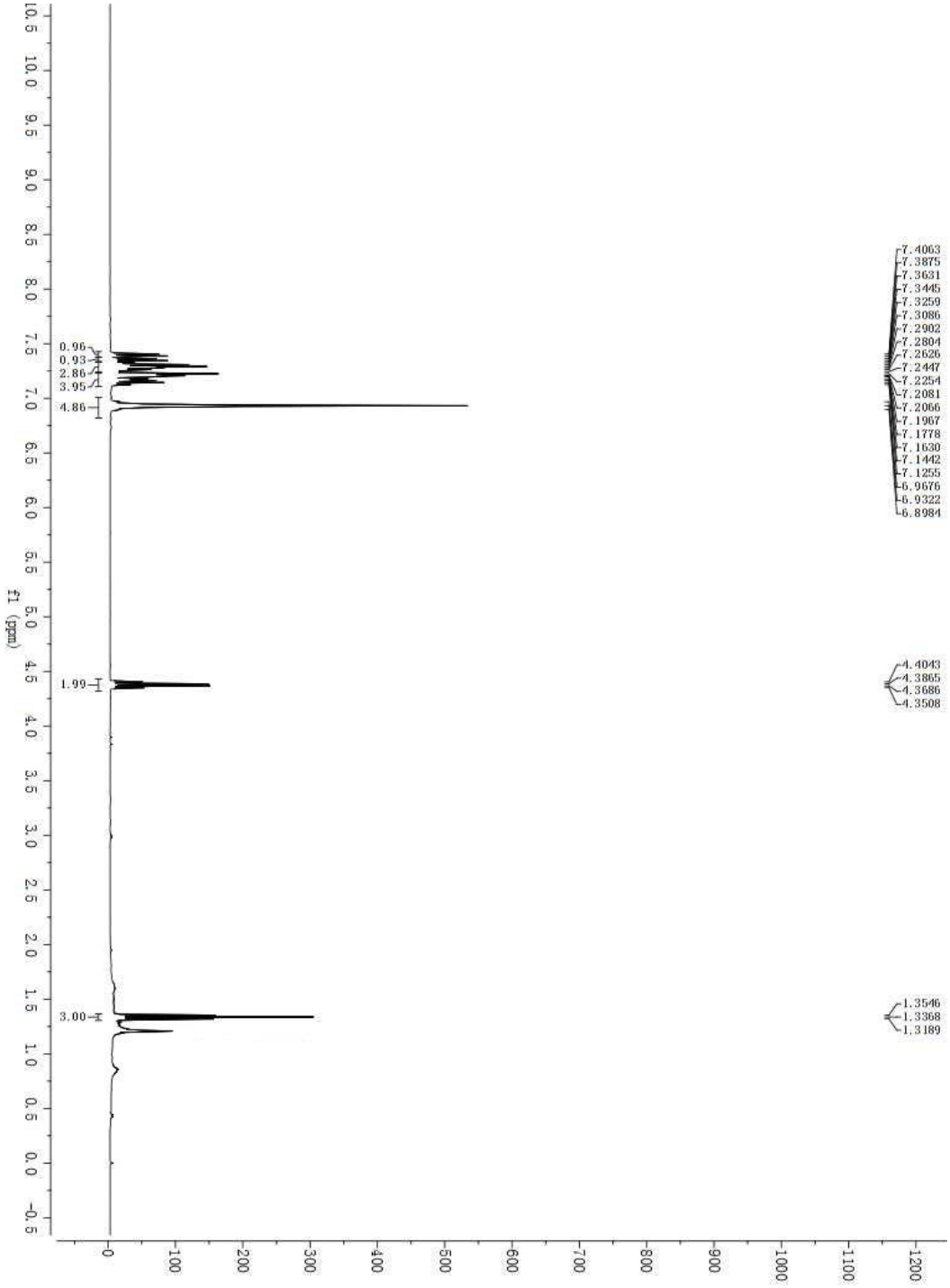
S = 1.055 Npar= 246

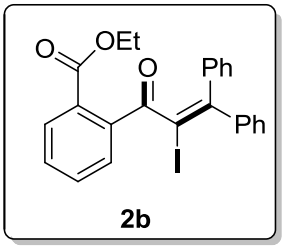

O
OMe
O
Ph
Ph
2a
7.3683
7.3496
7.3229
7.3063
7.2877
7.2779
7.2675
7.2609
7.2417
7.2060
7.1879
7.1691
7.1628
7.1422
7.1238
6.9473
6.9351
6.9268
6.9122
1.96
3.05
3.99
4.91
3.00
3.8999
f1 (ppm)


O
OMe
O
Ph
Ph
I
2a
193.3131
168.4831
158.5732
144.7615
139.6477
136.6863
132.1290
131.0164
130.3712
130.0954
129.6581
128.8032
128.6431
128.5906
128.2246
127.9719
101.3450
77.3181
76.9999
76.6820
53.0324
f1 (ppm)

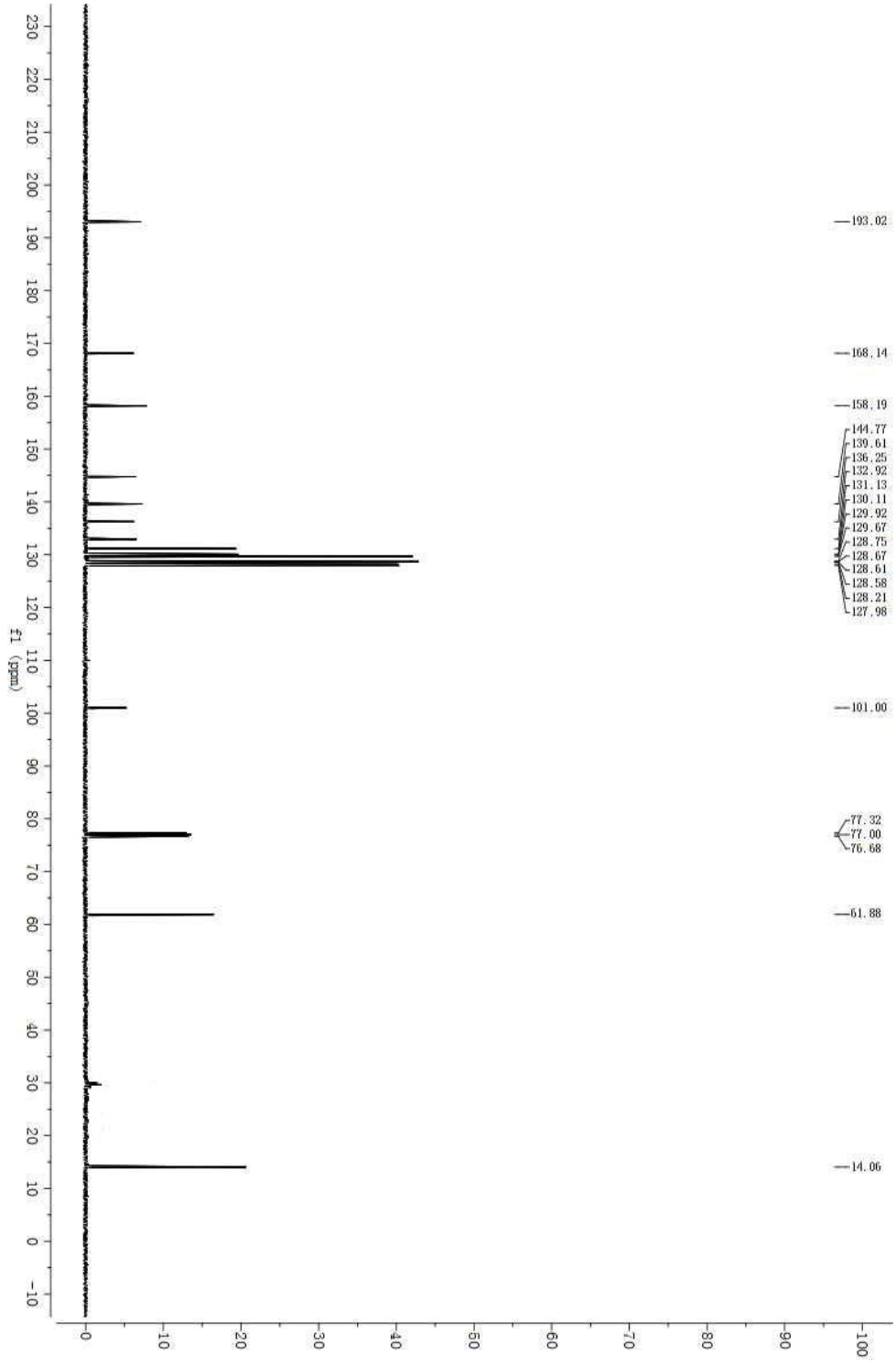

O
OEt
O
Ph
Ph
I

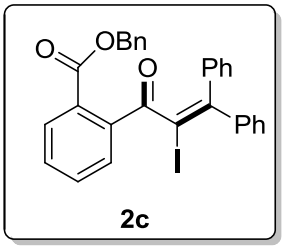
2b


f1 (ppm)
0.96
0.93
2.86
3.95
4.86
1.99
3.00
7.4063
7.3875
7.3631
7.3445
7.3259
7.3086
7.2902
7.2804
7.2626
7.2447
7.2254
7.2081
7.2066
7.1967
7.1778
7.1630
7.1442
7.1255
6.9676
6.9322
6.8984
4.4043
4.3865
4.3686
4.3508
1.3546
1.3368
1.3189

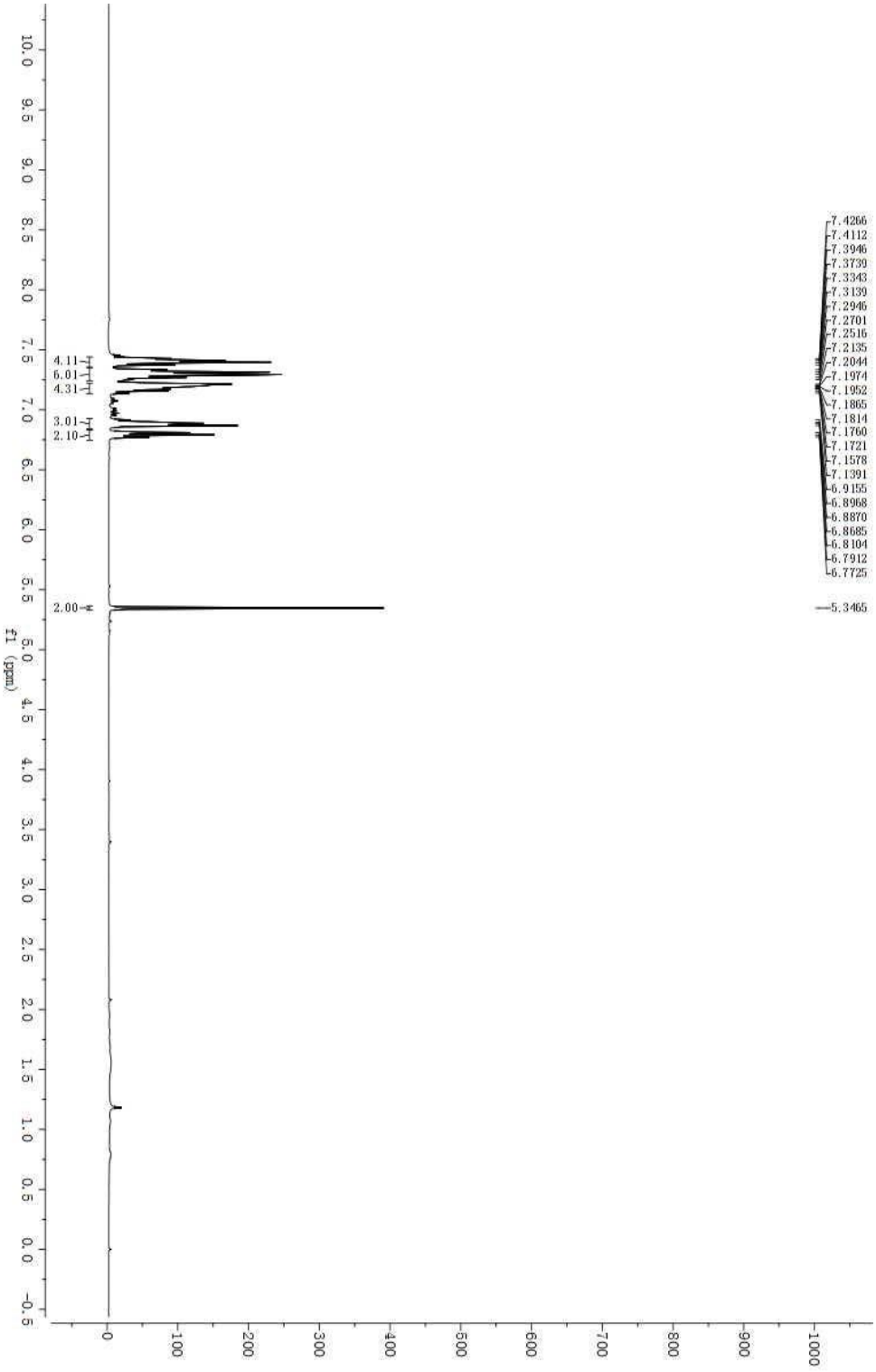

O
OEt
O
Ph
Ph
I

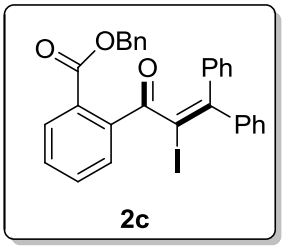
2b


193.02
168.14
158.19
144.77
139.61
136.25
132.92
131.13
130.11
129.92
129.67
128.75
128.67
128.61
128.58
128.21
127.98
101.00
77.32
77.00
76.68
61.88
14.06
f1 (ppm)

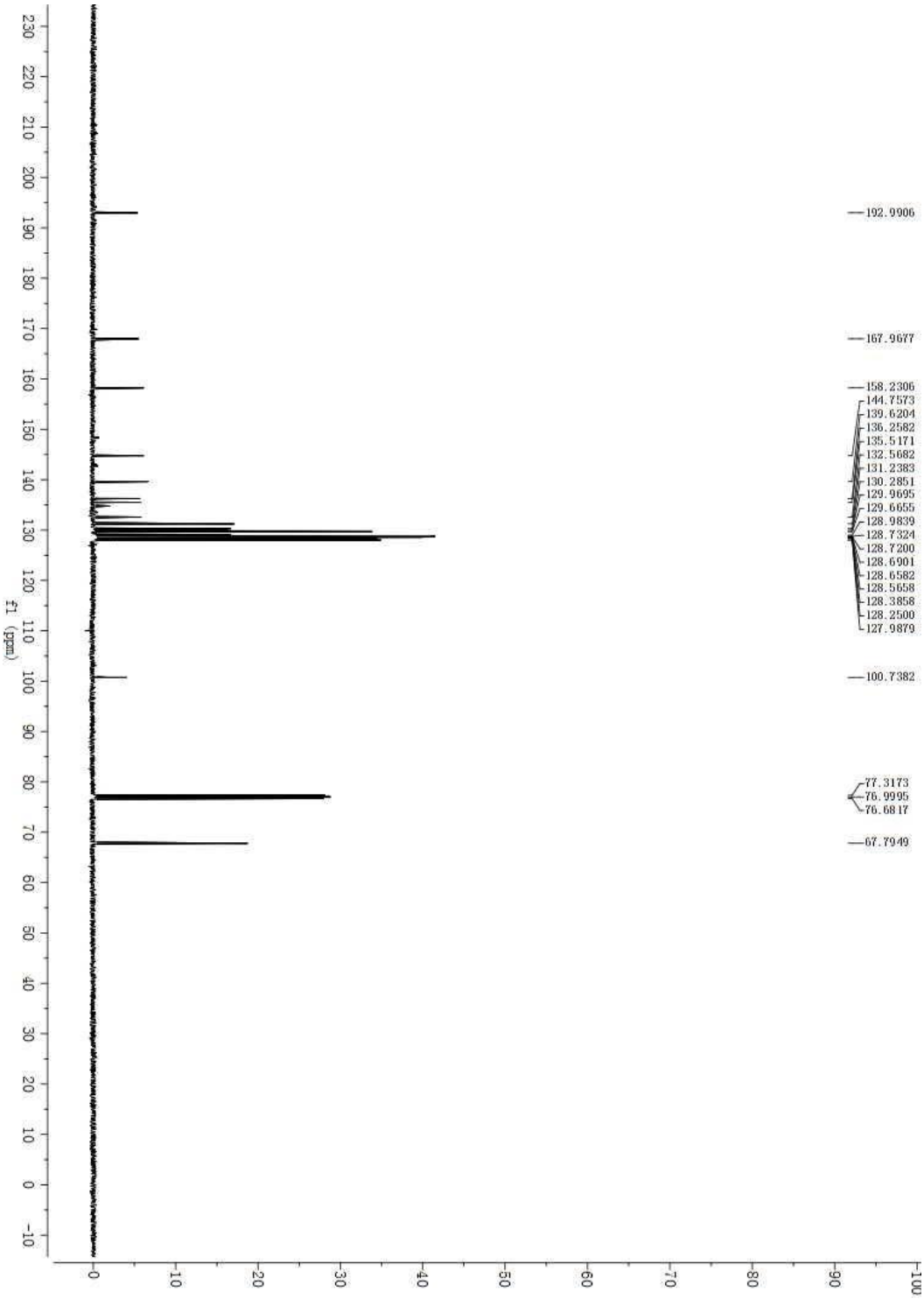

O
OBn
O
Ph
Ph

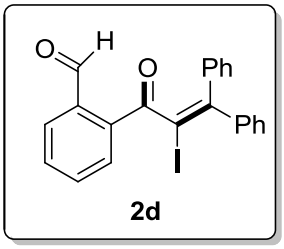
2c


4.11
6.01
4.31
3.01
2.10
2.00
f1 (ppm)
7.4266
7.4112
7.3946
7.3739
7.3343
7.3139
7.2946
7.2701
7.2516
7.2135
7.2044
7.1974
7.1952
7.1865
7.1814
7.1760
7.1721
7.1578
7.1391
6.9155
6.8968
6.8870
6.8685
6.8104
6.7912
6.7725
5.3465

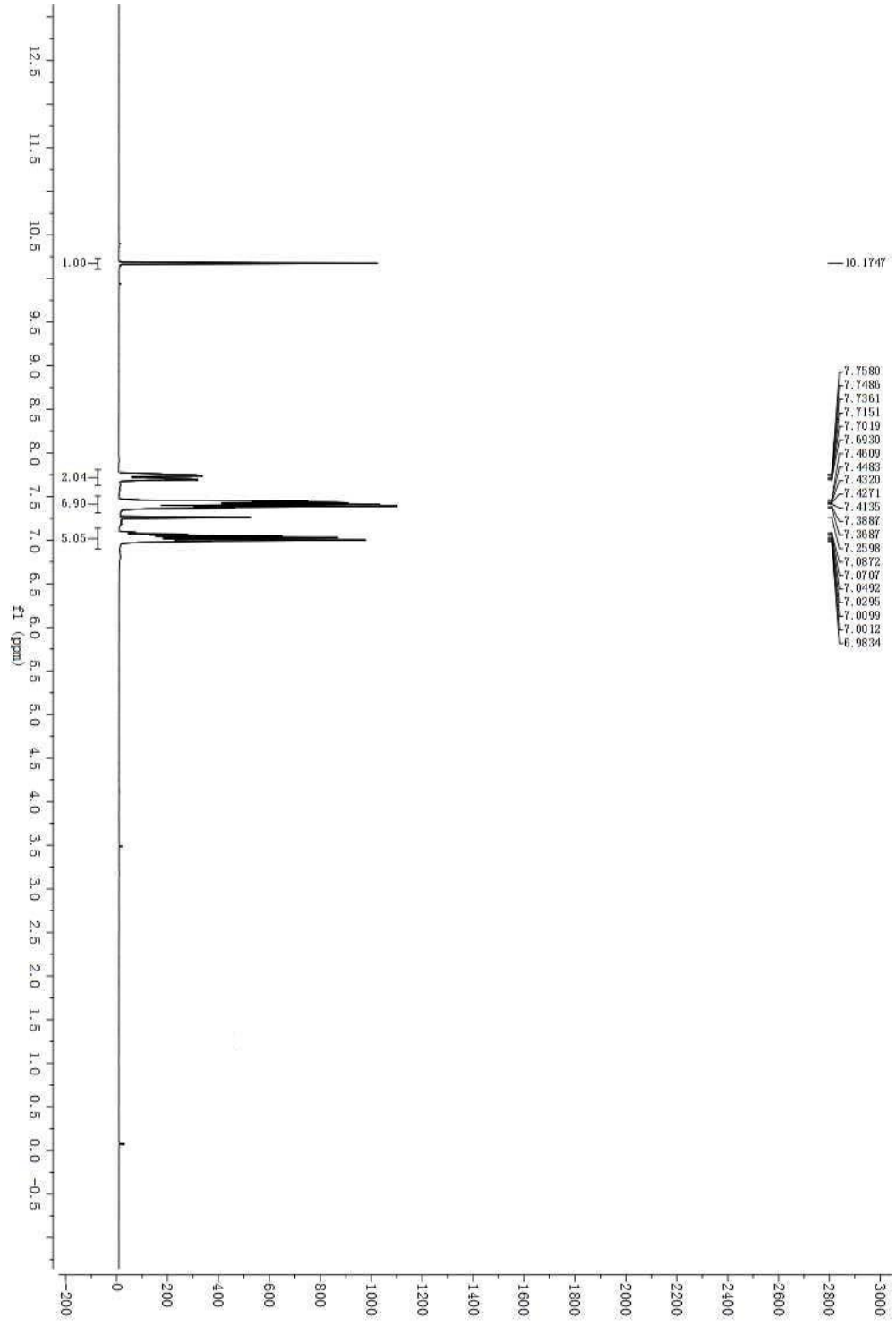

O
OBn
O
Ph
Ph

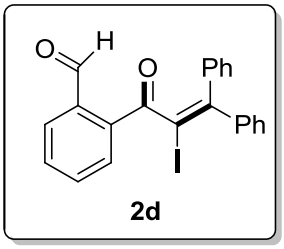
2c


192.9906
167.9677
158.2306
144.7573
139.6204
136.2582
135.5171
132.5682
131.2383
130.2851
129.9695
129.6655
128.9839
128.7324
128.7200
128.6901
128.6582
128.5658
128.3858
128.2500
127.9879
100.7382
77.3173
76.9995
76.6817
67.7949
f1 (ppm)

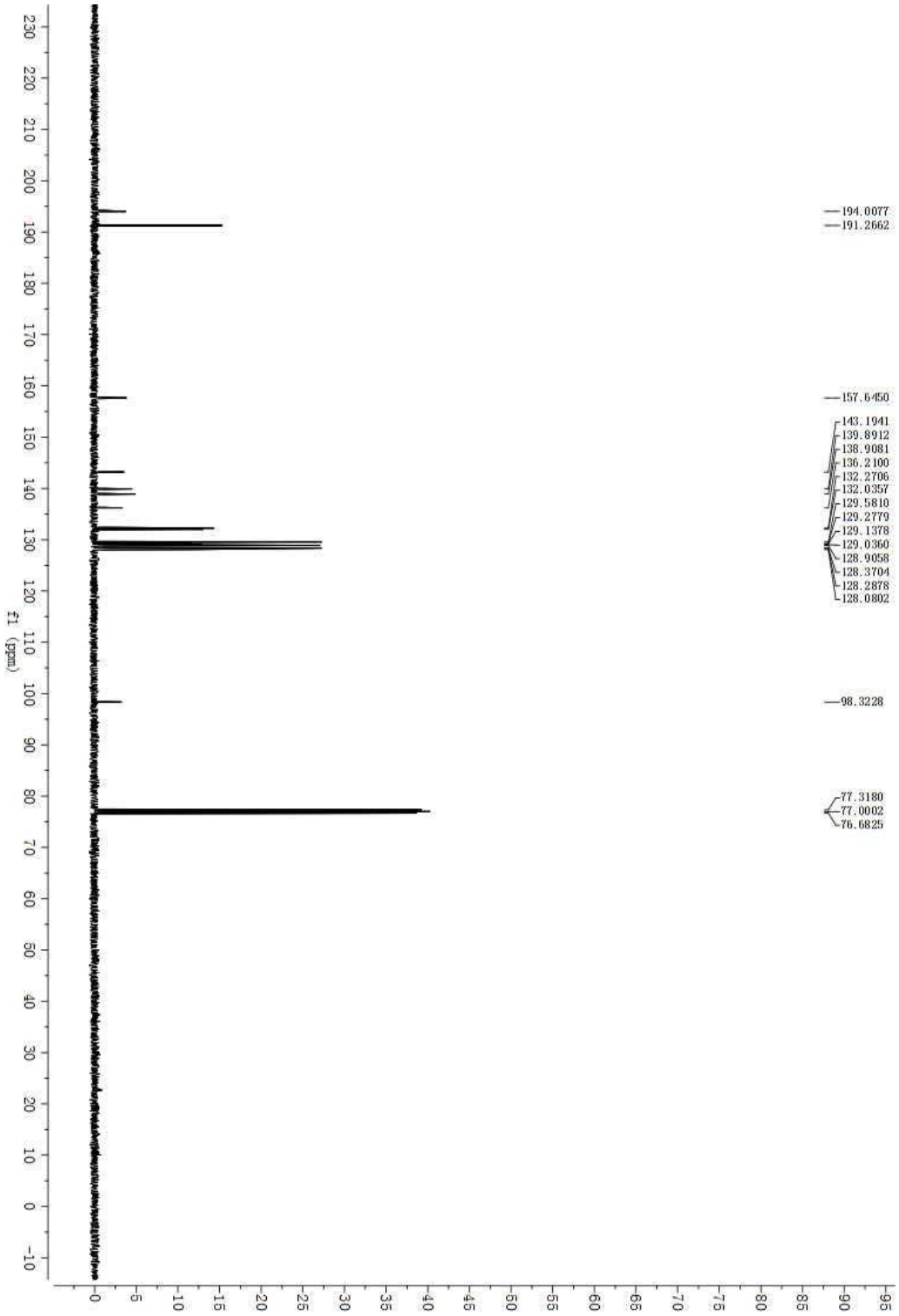

O
H
O
Ph
Ph
I

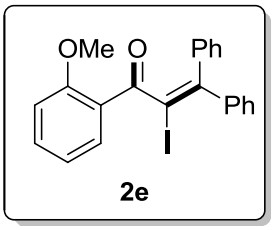
2d


1.00
2.04
6.90
5.05
10.1747
7.7580
7.7486
7.7361
7.7151
7.7019
7.6930
7.4609
7.4483
7.4320
7.4271
7.4135
7.3887
7.3687
7.2598
7.0872
7.0707
7.0492
7.0295
7.0099
7.0012
6.9834
f1 (ppm)

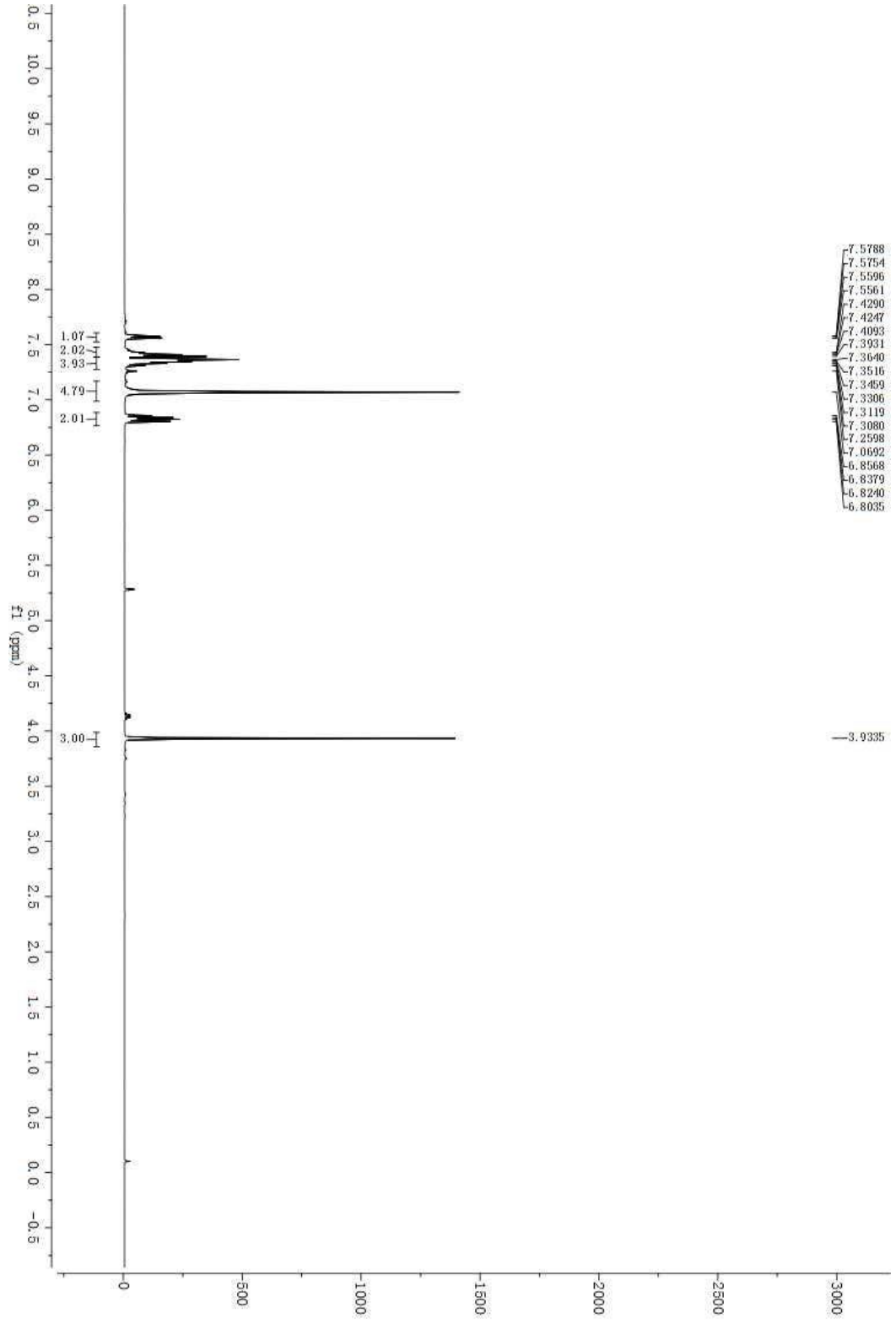

O
H
O
Ph
Ph
I

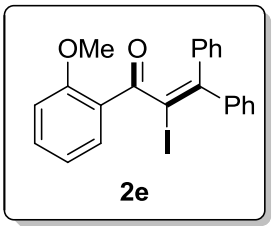
2d


194.0077
191.2662
157.6450
143.1941
139.8912
138.9081
136.2100
132.2706
132.0357
129.5810
129.2779
129.1378
129.0360
128.9058
128.3704
128.2878
128.0802
98.3228
77.3180
77.0002
76.6825
f1 (ppm)

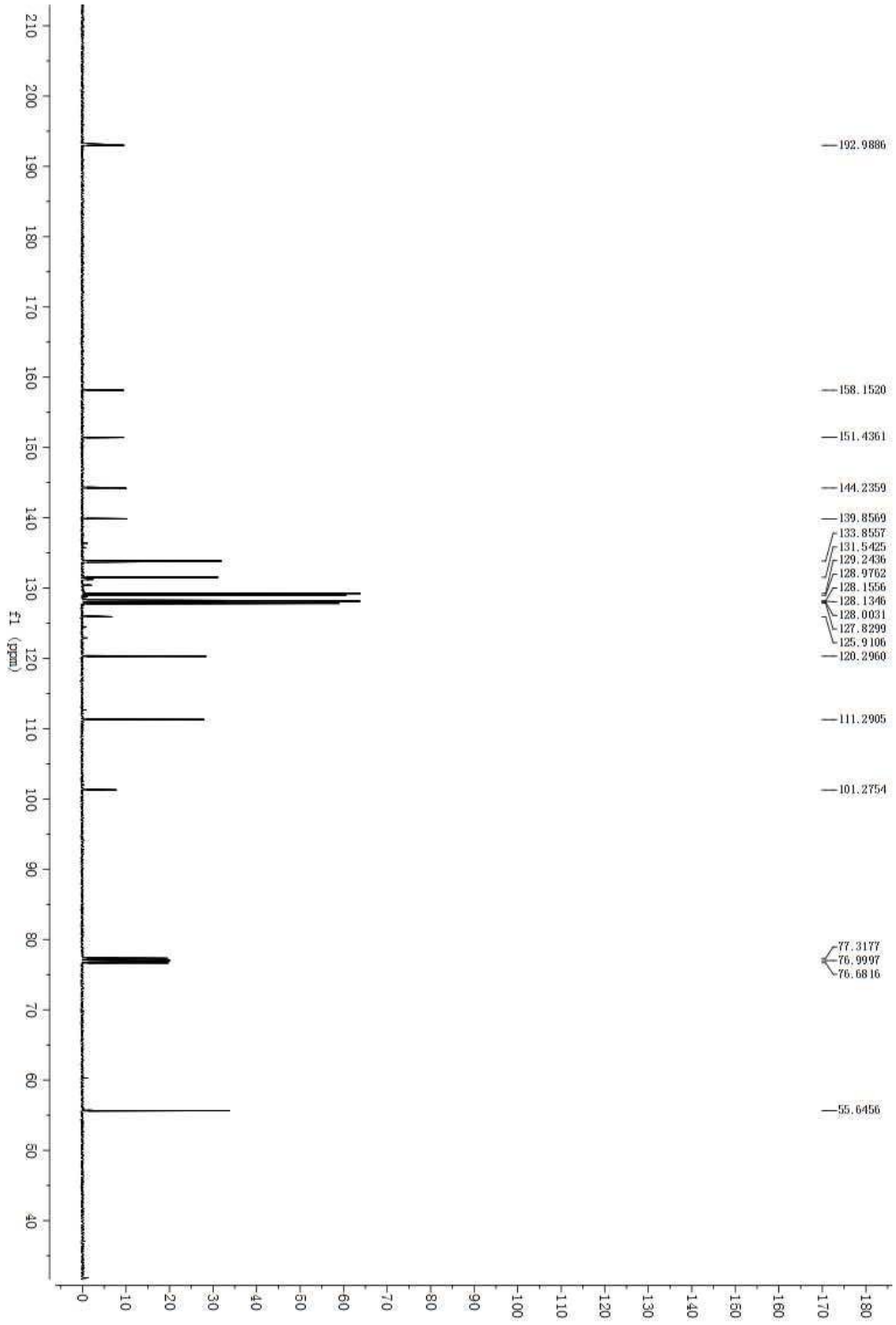

OMe
O
Ph
Ph
I

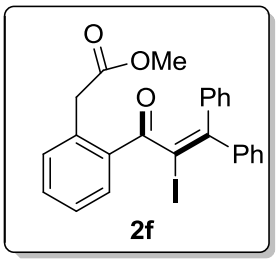
2e


1.07
2.02
3.93
4.79
2.01
3.00
7.5788
7.5754
7.5596
7.5561
7.4290
7.4247
7.4093
7.3931
7.3640
7.3516
7.3459
7.3306
7.3119
7.3080
7.2598
7.0692
6.8568
6.8379
6.8240
6.8035
3.9335
f1 (ppm)

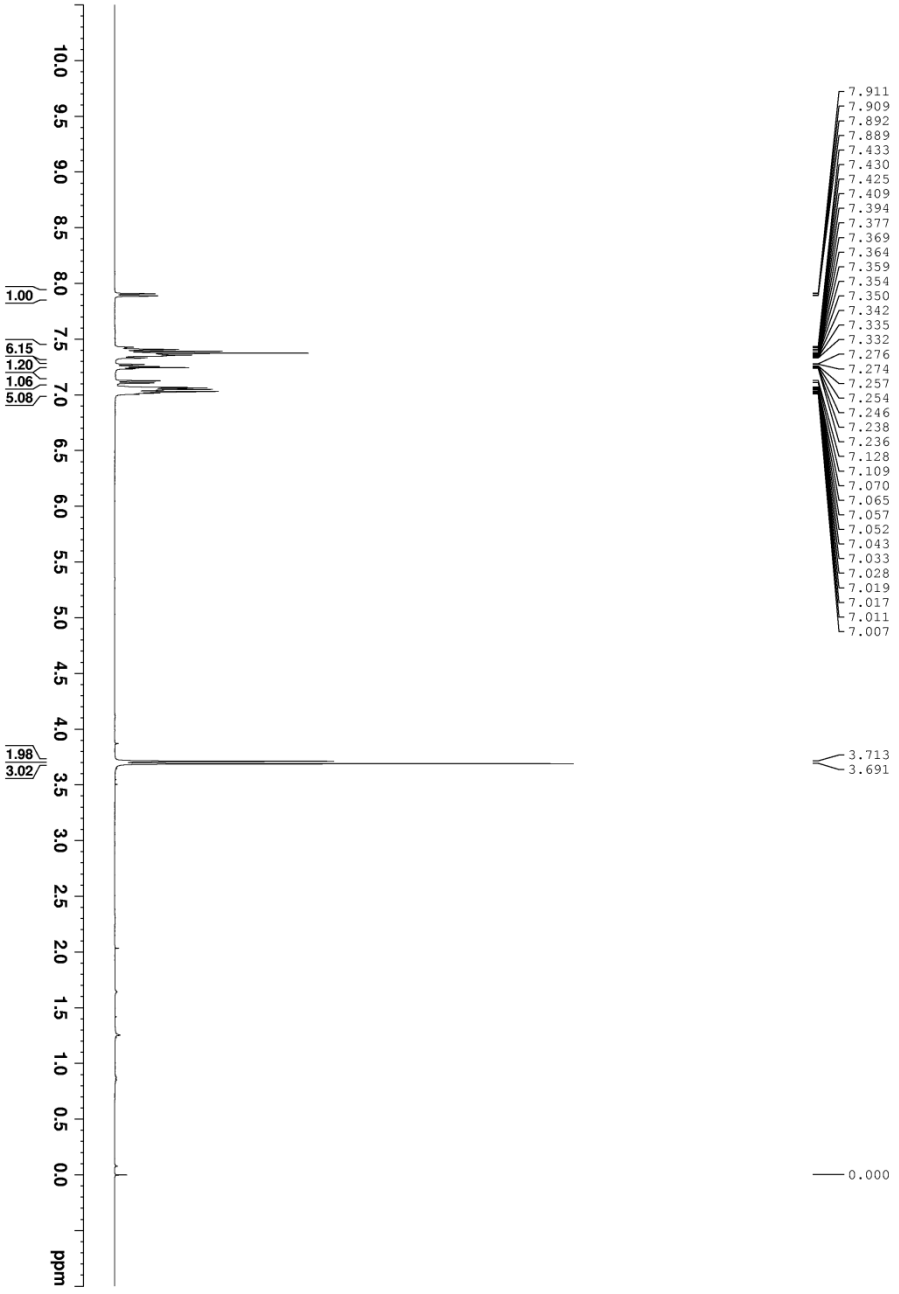

OMe
O
Ph
Ph
I

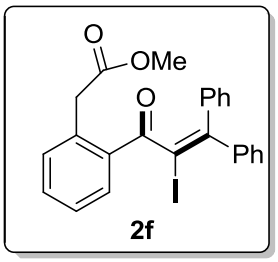
2e


f1 (ppm)
192.9886
158.1520
151.4361
144.2359
139.8569
133.8557
131.5425
129.2436
128.9762
128.1556
128.1346
128.0031
127.8299
125.9106
120.2960
111.2905
101.2754
77.3177
76.9997
76.6816
55.6456

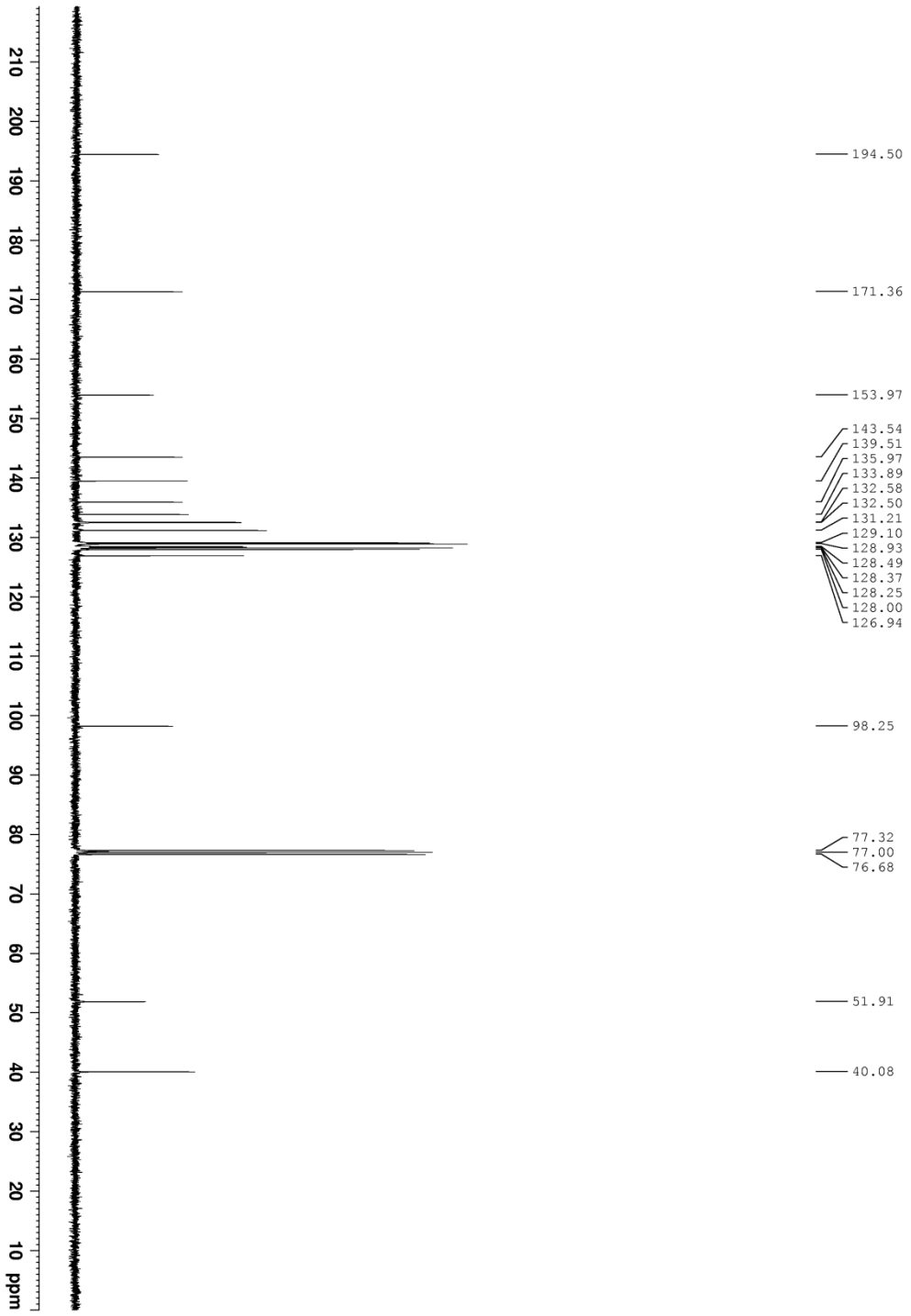

O
OMe
O
Ph
Ph
I

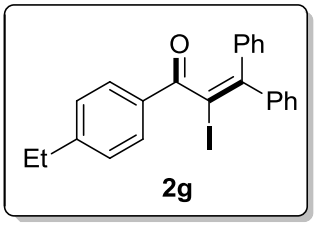
2f


10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
6.15
1.20
1.06
5.08
1.98
3.02
7.911
7.909
7.892
7.889
7.433
7.430
7.425
7.409
7.394
7.377
7.369
7.364
7.359
7.354
7.350
7.342
7.335
7.332
7.276
7.274
7.257
7.254
7.246
7.238
7.236
7.128
7.109
7.070
7.065
7.057
7.052
7.043
7.033
7.028
7.019
7.017
7.011
7.007
3.713
3.691
0.000

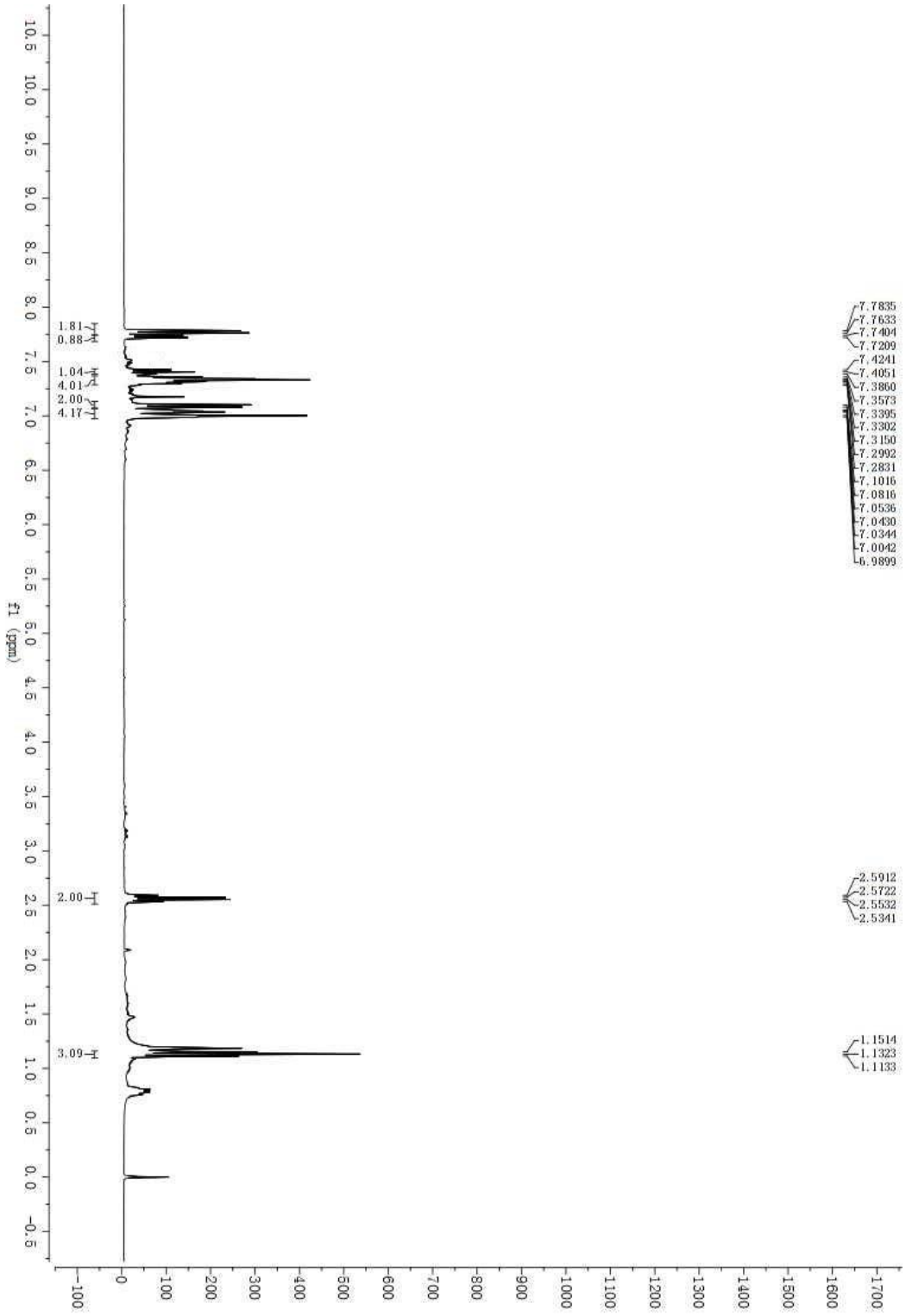

O
OMe
O
Ph
Ph
I

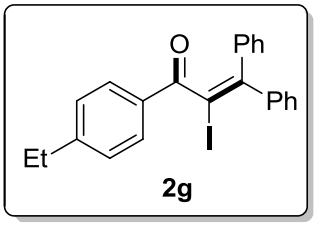
2f


194.50
171.36
153.97
143.54
139.51
135.97
133.89
132.58
132.50
131.21
129.10
128.93
128.49
128.37
128.25
128.00
126.94
98.25
77.32
77.00
76.68
51.91
40.08
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

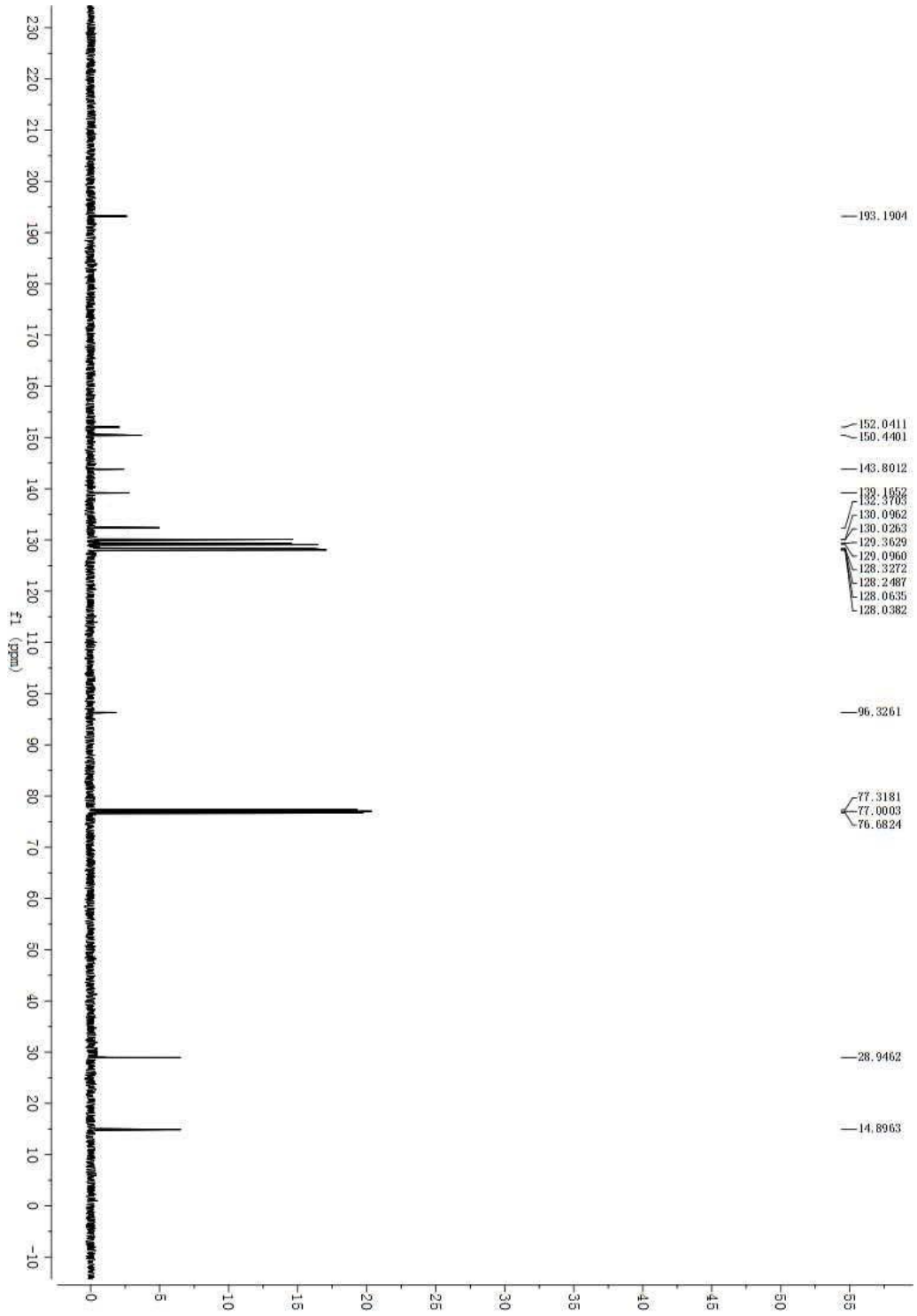

O
Ph
Ph
I
Et

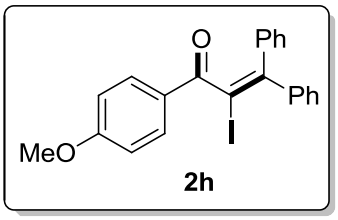
2g


1.81
0.88
1.04
4.01
2.00
4.17
2.00
3.09
f1 (ppm)
7.7835
7.7633
7.7404
7.7209
7.4241
7.4051
7.3860
7.3573
7.3395
7.3302
7.3150
7.2992
7.2831
7.1016
7.0816
7.0536
7.0430
7.0344
7.0042
6.9899
2.5912
2.5722
2.5532
2.5341
1.1514
1.1323
1.1133

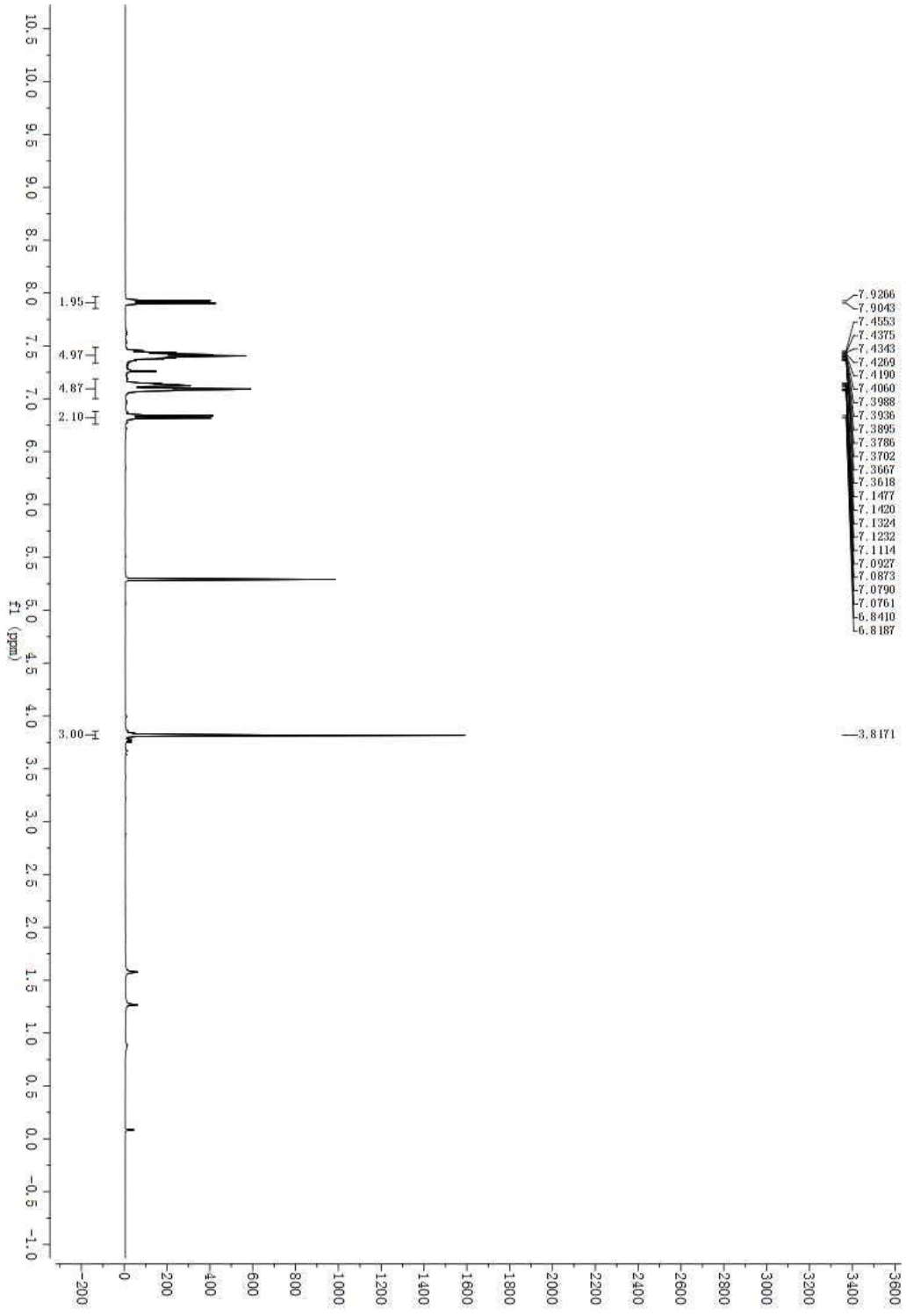

O
Ph
Ph
I
Et

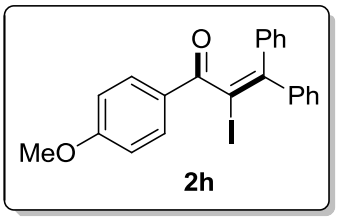
2g


193.1904
152.0411
150.4401
143.8012
139.1652
132.3703
130.0962
130.0263
129.3629
129.0960
128.3272
128.2487
128.0635
128.0382
96.3261
77.3181
77.0003
76.6824
28.9462
14.8963
f1 (ppm)

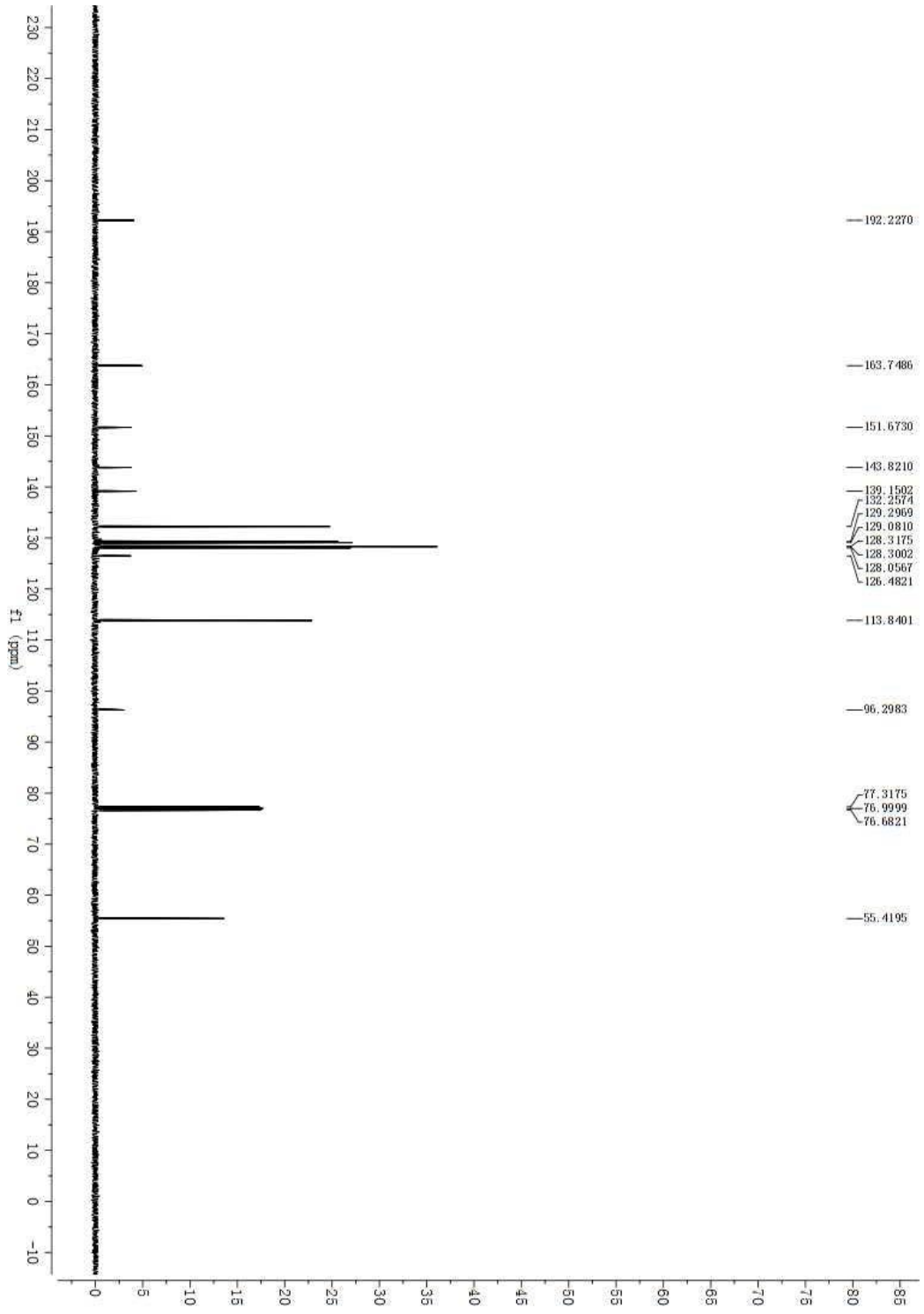

O
Ph
Ph
I
MeO

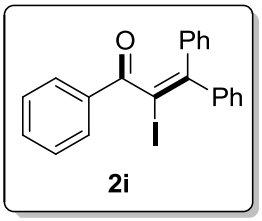
2h


1.95
4.97
4.87
2.10
3.00
f1 (ppm)
7.9266
7.9043
7.4553
7.4375
7.4343
7.4269
7.4190
7.4060
7.3988
7.3936
7.3895
7.3786
7.3702
7.3667
7.3618
7.1477
7.1420
7.1324
7.1232
7.1114
7.0927
7.0873
7.0790
7.0761
6.8410
6.8187
3.8171

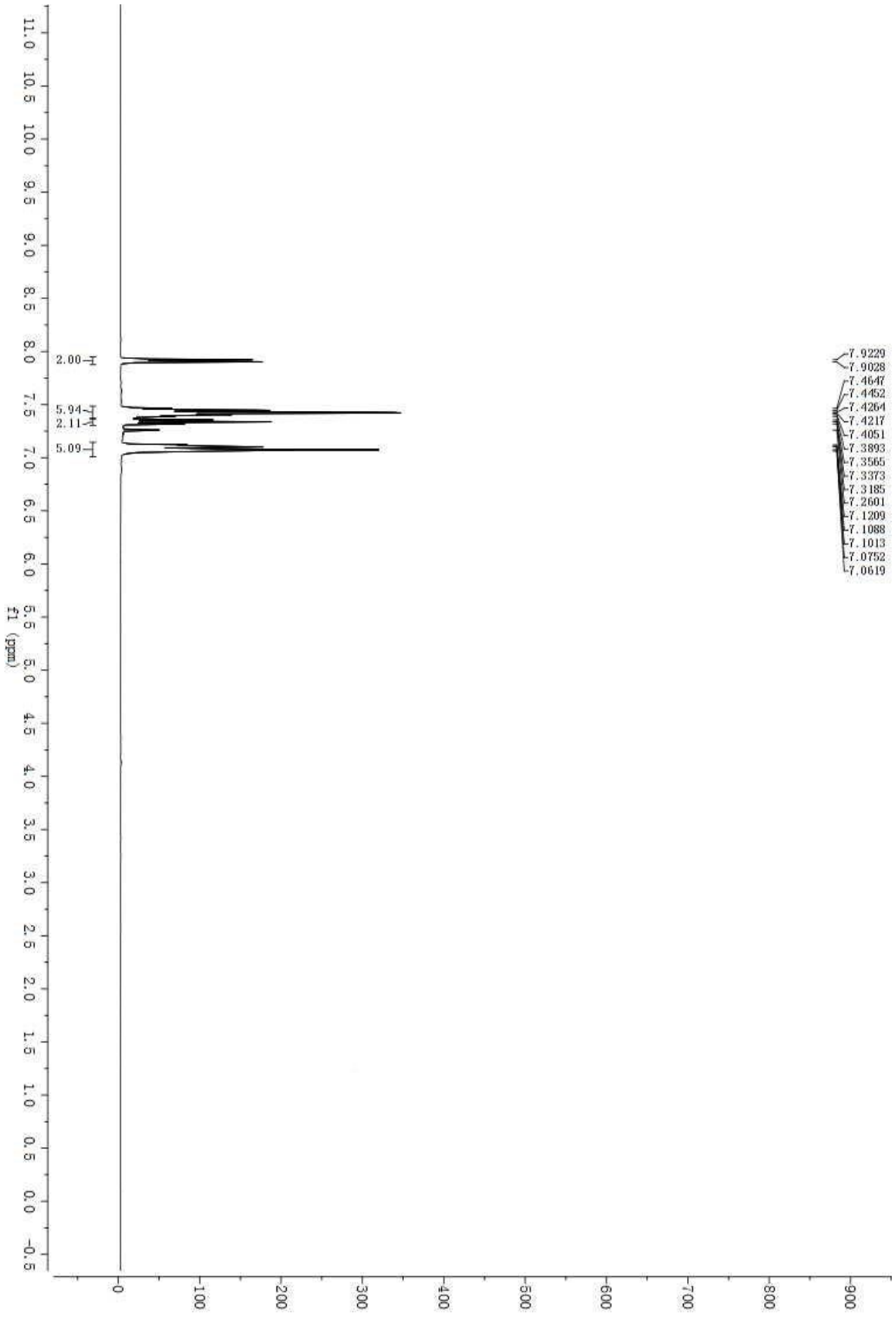

O
Ph
Ph
I
MeO

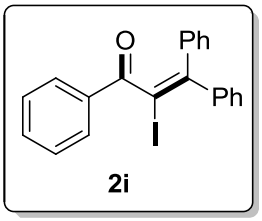
2h


192.2270
163.7486
151.6730
143.8210
139.1502
132.2574
129.2969
129.0810
128.3175
128.3002
128.0567
126.4821
113.8401
96.2983
77.3175
76.9999
76.6821
55.4195
f1 (ppm)

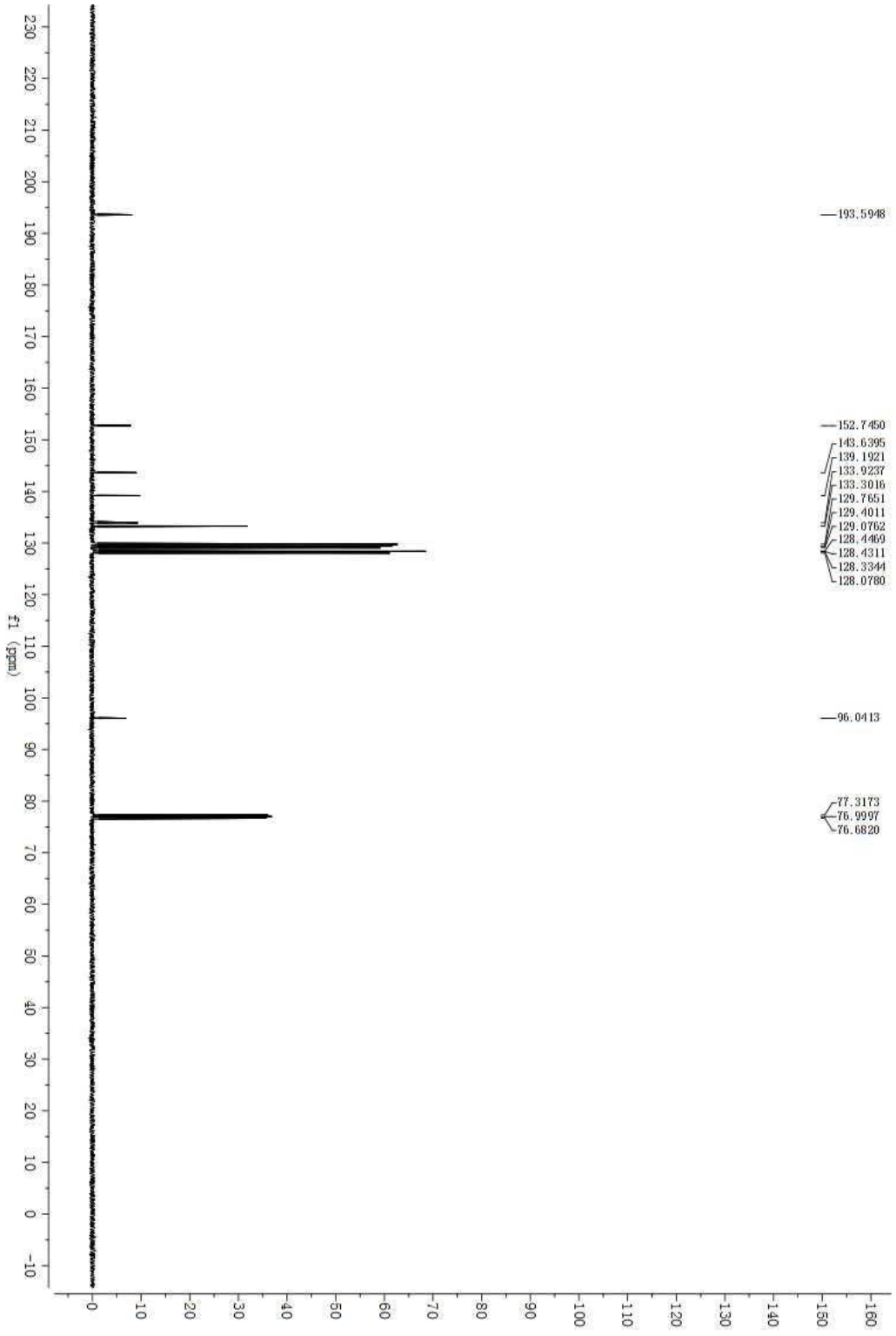

O
Ph
Ph
I

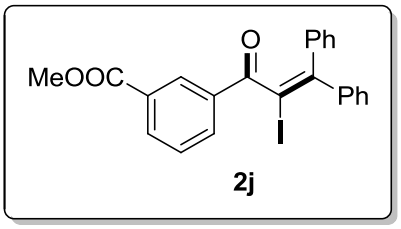
2i


2.00
5.94
2.11
5.09
7.9229
7.9028
7.4647
7.4452
7.4264
7.4217
7.4051
7.3893
7.3565
7.3373
7.3185
7.2601
7.1209
7.1088
7.1013
7.0752
7.0619
f1 (ppm)

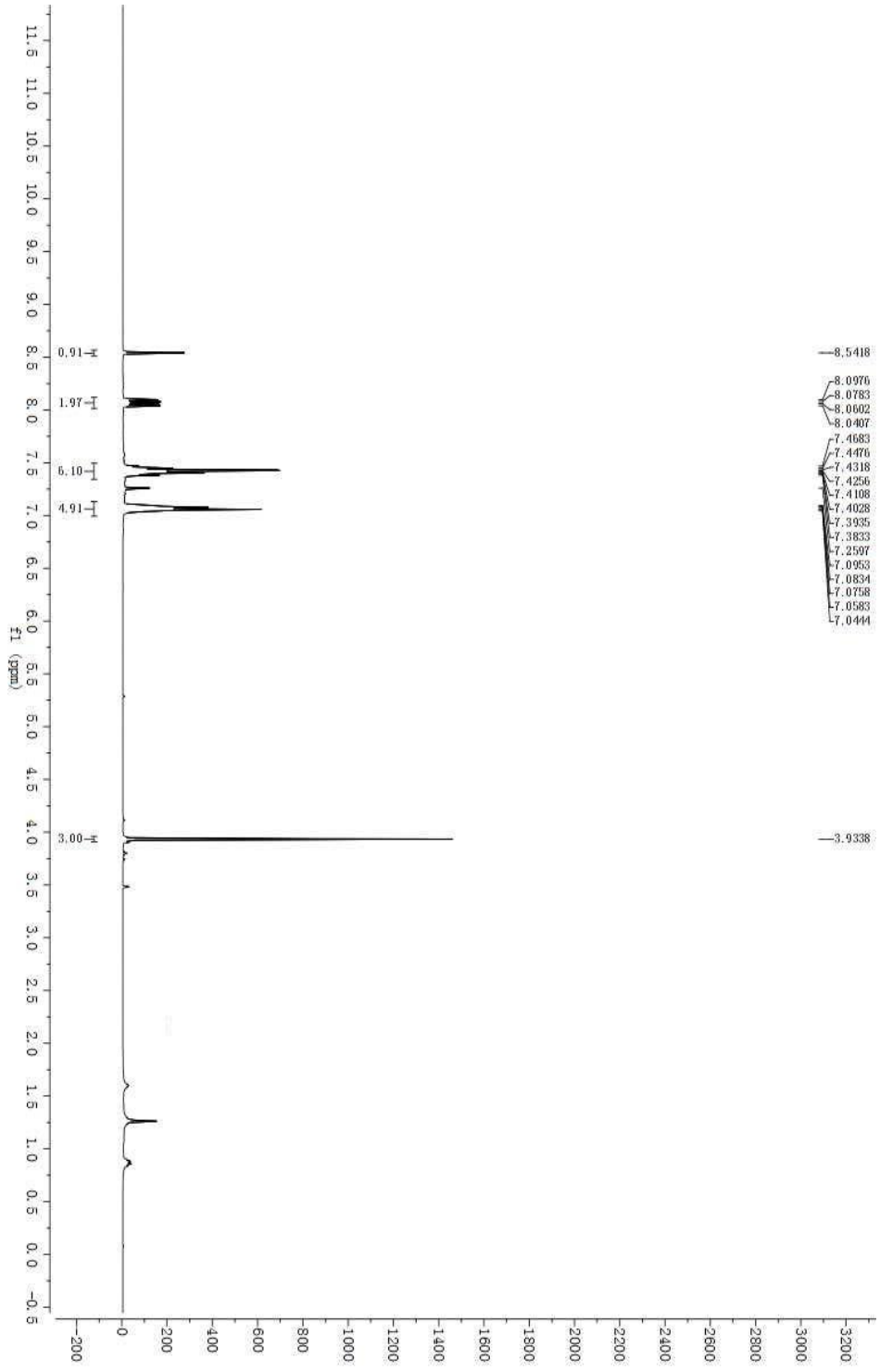

O
Ph
Ph
I

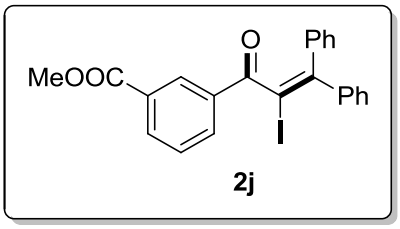
2i


193.5948
152.7450
143.6395
139.1921
133.9237
133.3016
129.7651
129.4011
129.0762
128.4469
128.4311
128.3344
128.0780
96.0413
77.3173
76.9997
76.6820
f1 (ppm)

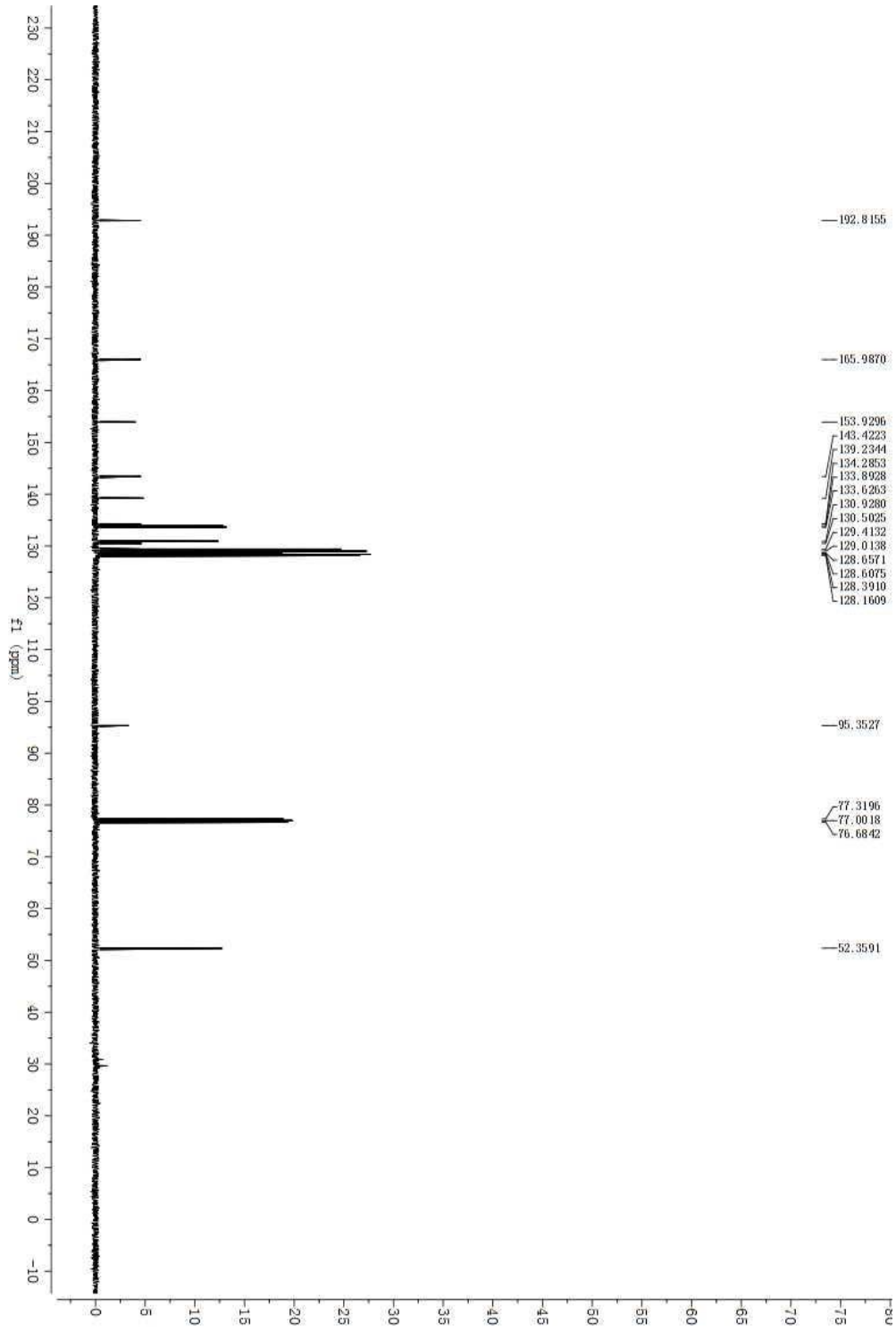

MeOOC
O
Ph
Ph
I

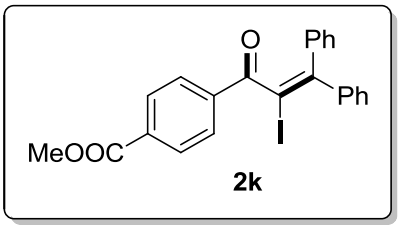
2j


0.91
1.97
6.10
4.91
3.00
8.5418
8.0976
8.0783
8.0602
8.0407
7.4683
7.4476
7.4318
7.4256
7.4108
7.4028
7.3935
7.3833
7.2597
7.0953
7.0834
7.0758
7.0583
7.0444
3.9338
f1 (ppm)

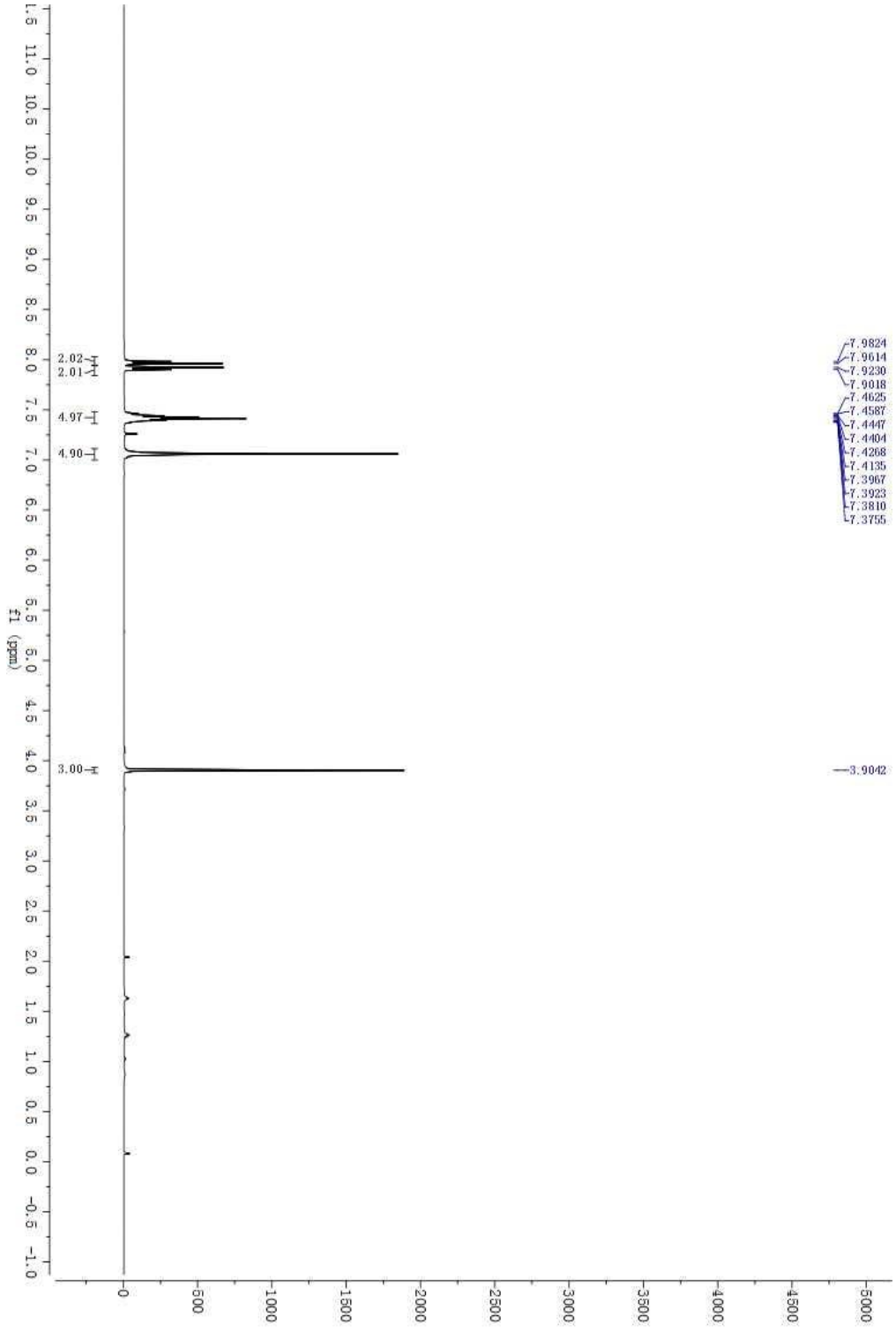

MeOOC
O
Ph
Ph
I

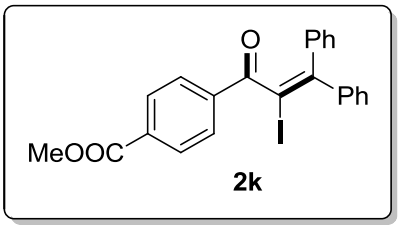
2j


192.8155
165.9870
153.9296
143.4223
139.2344
134.2853
133.8928
133.6263
130.9280
130.5025
129.4132
129.0138
128.6571
128.6075
128.3910
128.1609
95.3527
77.3196
77.0018
76.6842
52.3591
f1 (ppm)

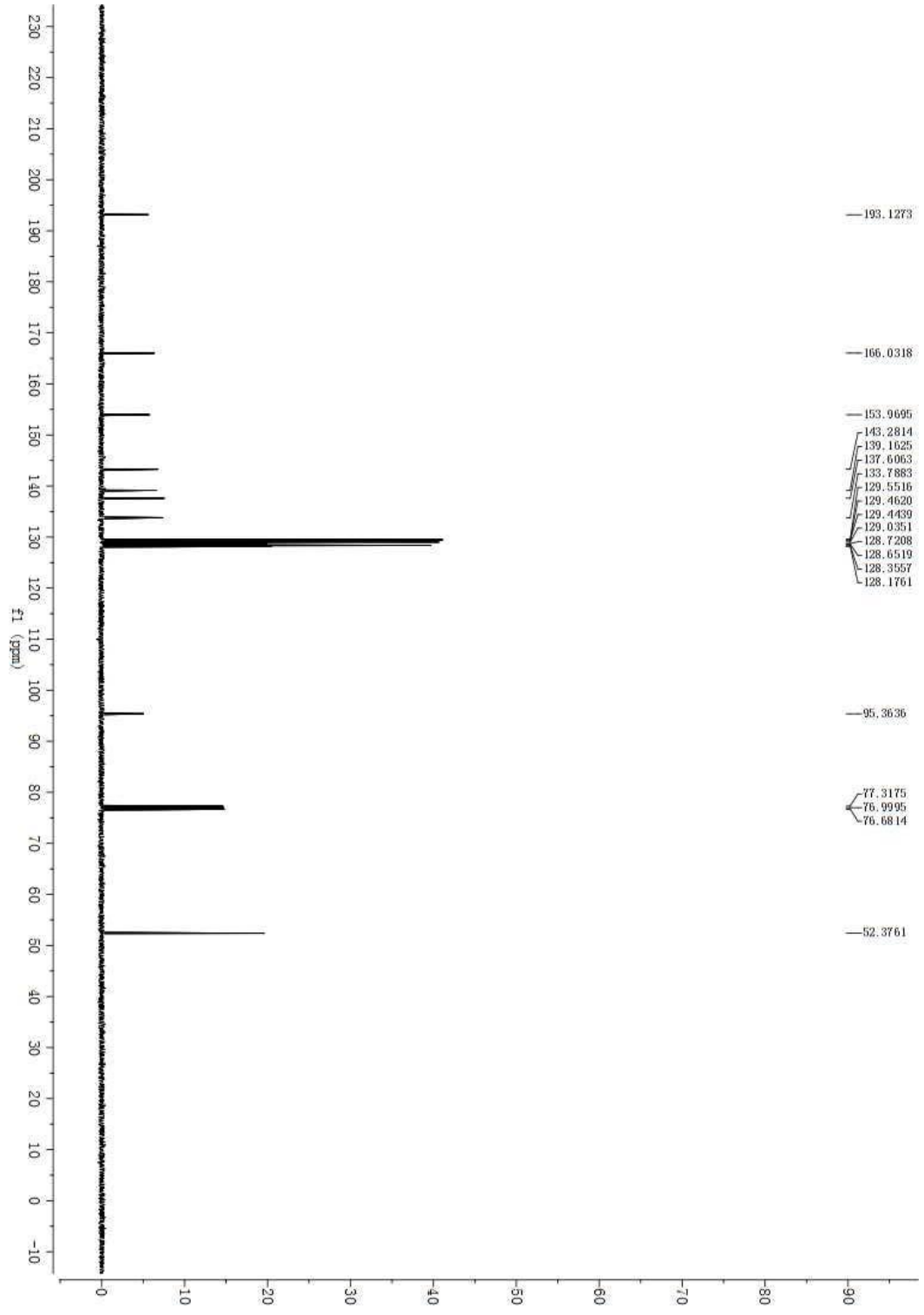

O
Ph
Ph
MeOOC

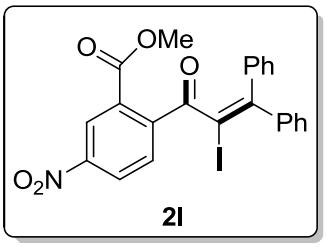
2k


2.02
2.01
4.97
4.90
3.00
7.9824
7.9614
7.9230
7.9018
7.4625
7.4587
7.4447
7.4404
7.4268
7.4135
7.3967
7.3923
7.3810
7.3755
3.9042
f1 (ppm)

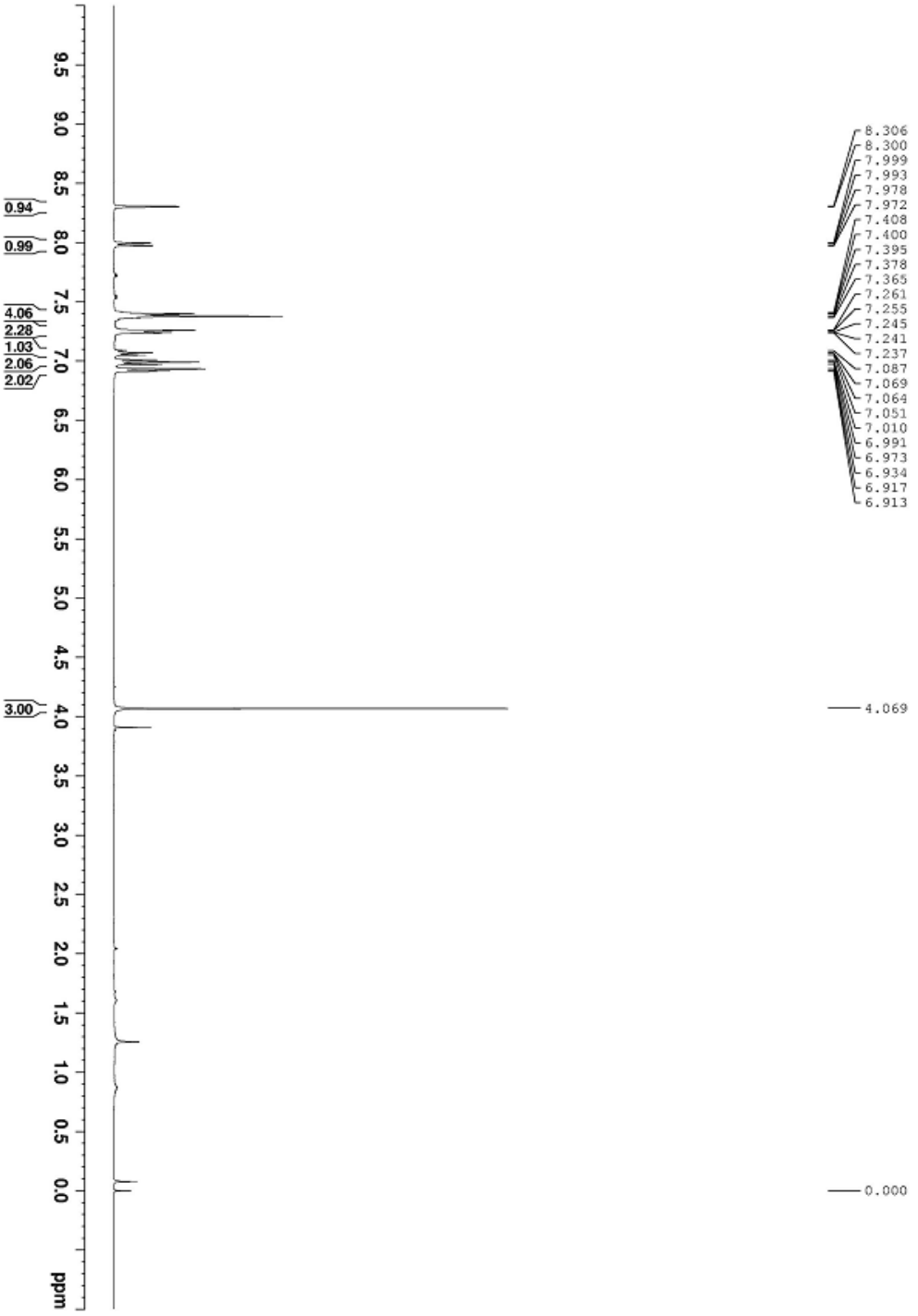

O
Ph
Ph
I
MeOOC

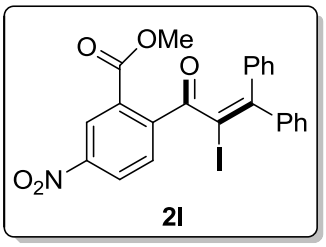
2k


193.1273
166.0318
153.9695
143.2814
139.1625
137.6063
133.7883
129.5516
129.4620
129.4439
129.0351
128.7208
128.6519
128.3557
128.1761
95.3636
77.3175
76.9995
76.6814
52.3761
f1 (ppm)

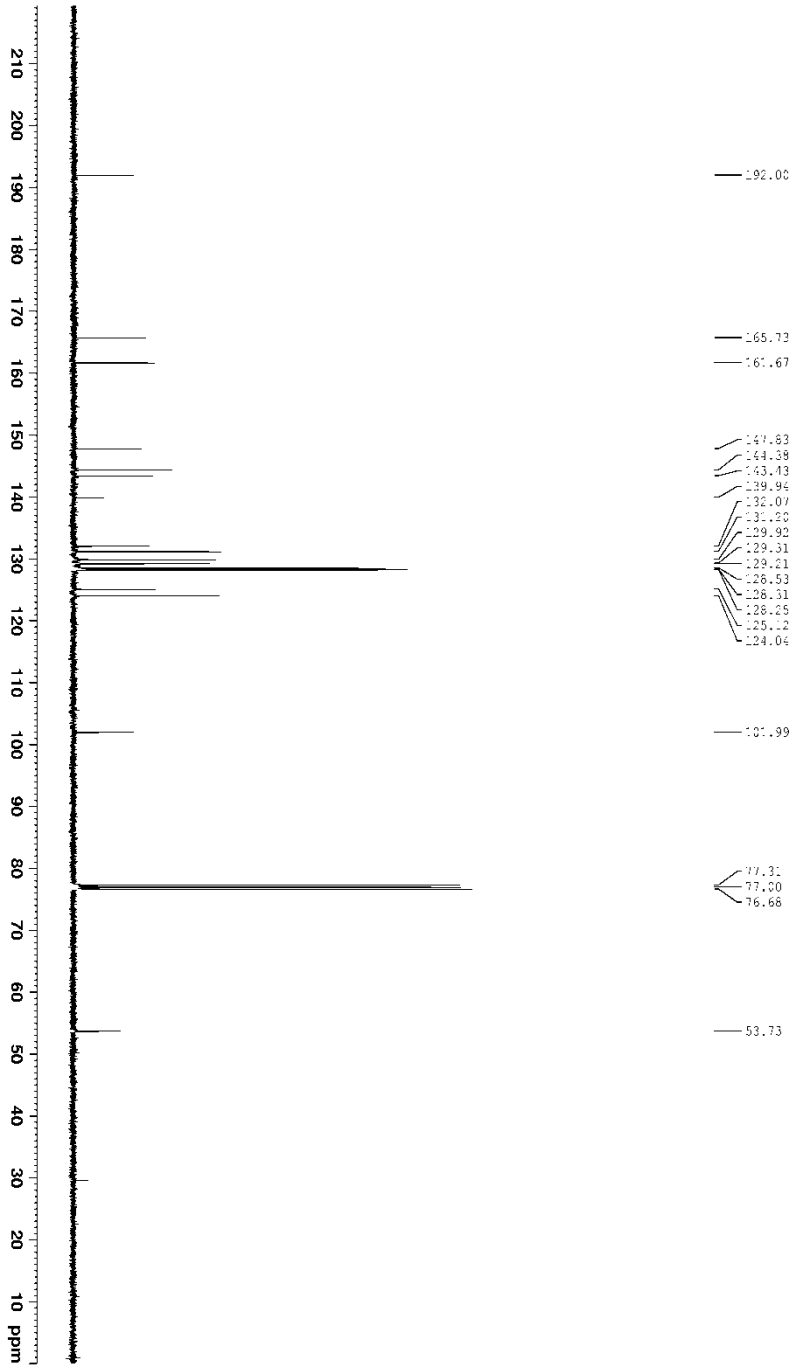

O
OMe
O
Ph
Ph
I
O2N

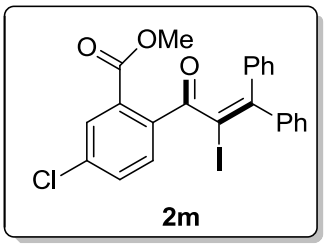
2l


0.94
0.99
4.06
2.28
1.03
2.06
2.02
3.00
ppm
8.306
8.300
7.999
7.993
7.978
7.972
7.408
7.400
7.395
7.378
7.365
7.261
7.255
7.245
7.241
7.237
7.087
7.069
7.064
7.051
7.010
6.991
6.973
6.934
6.917
6.913
4.069
0.000

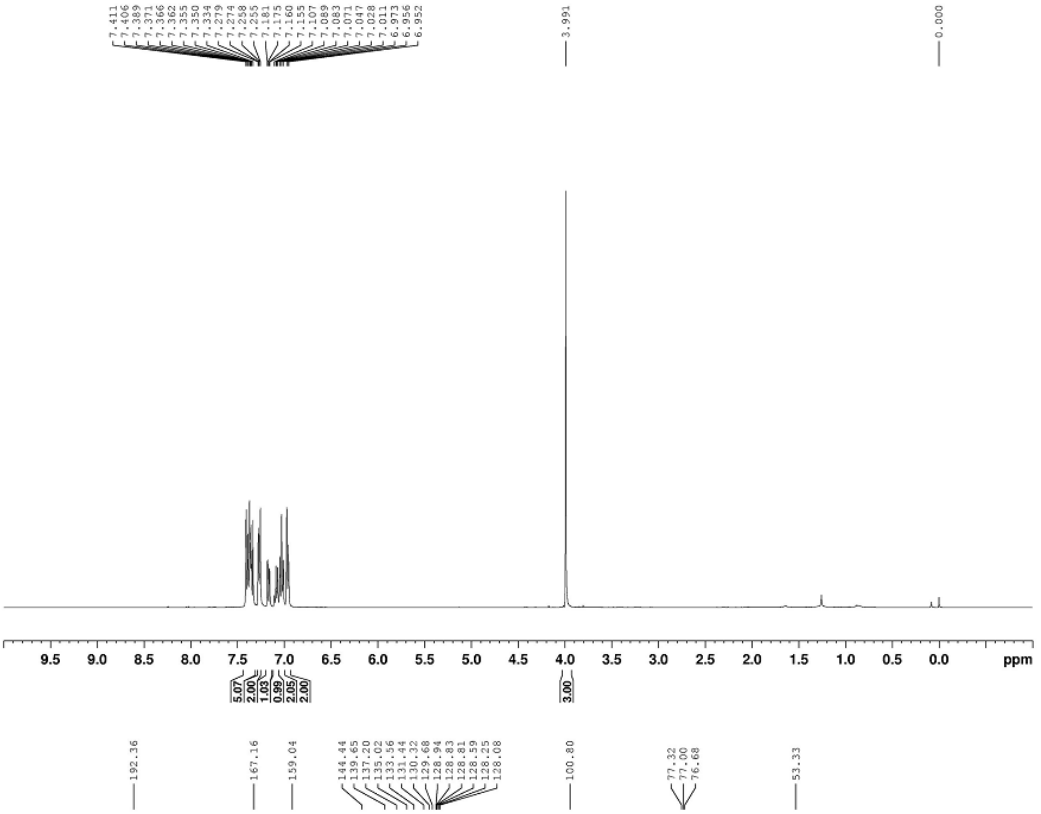

O
OMe
O
Ph
Ph
I
O2N

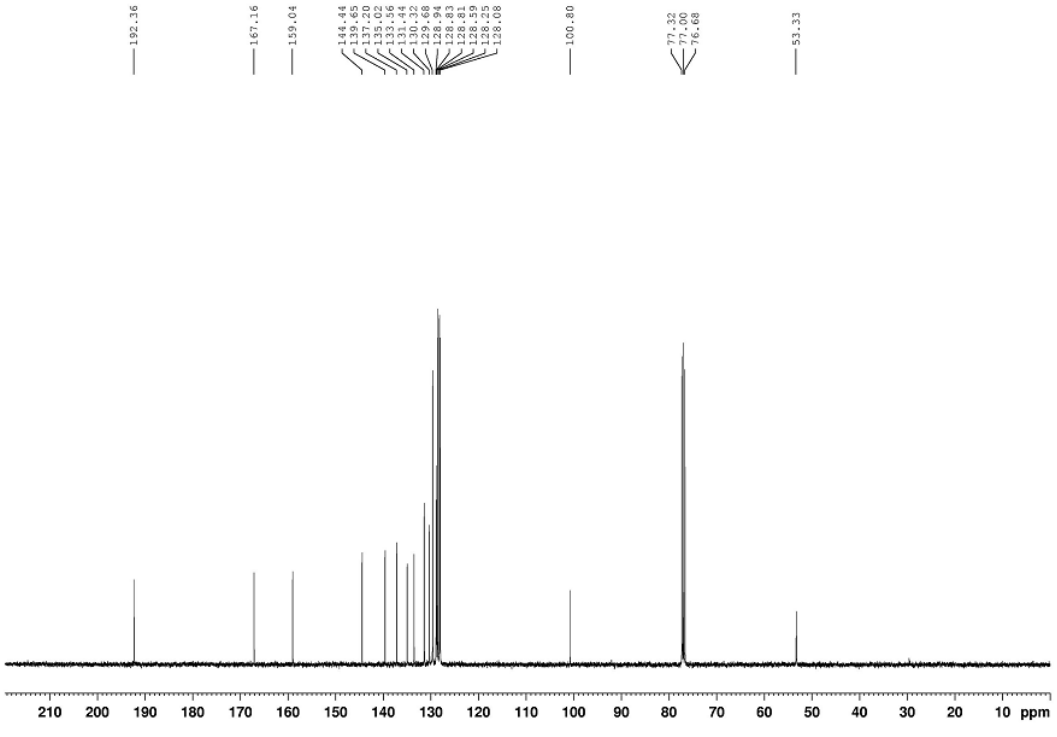
2l

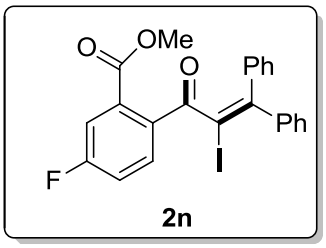

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
192.00
165.73
161.67
147.83
144.38
143.43
139.96
132.07
131.20
129.92
129.31
129.21
128.53
128.31
128.25
125.12
124.04
101.99
77.31
77.00
76.68
53.73


O
OMe
O
Ph
Ph
I
Cl

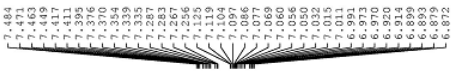
2m

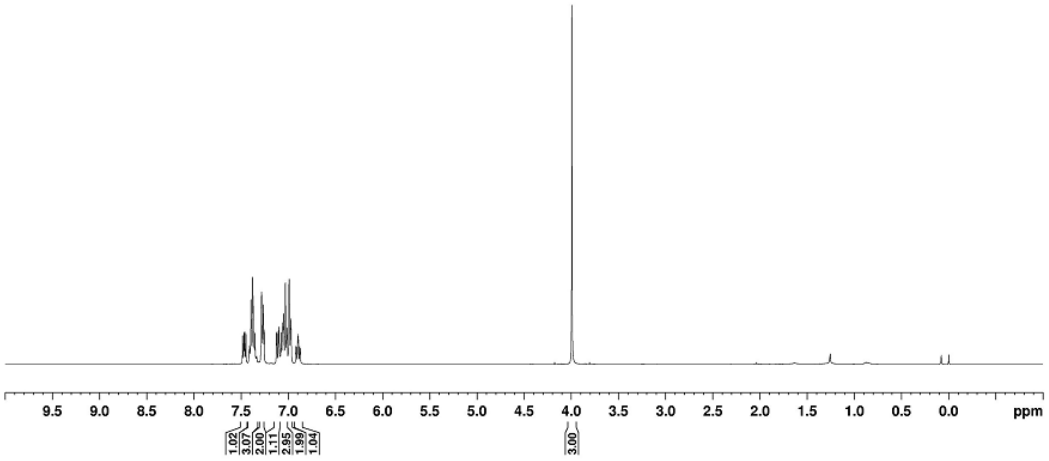

7.411
7.406
7.389
7.371
7.366
7.362
7.355
7.350
7.334
7.279
7.274
7.258
7.255
7.181
7.175
7.160
7.155
7.107
7.089
7.083
7.071
7.047
7.028
7.011
6.973
6.956
6.952
3.991
0.000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
5.07
2.00
1.03
0.99
2.05
2.00
3.00

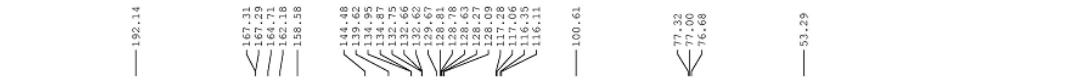

192.36
167.16
159.04
144.44
139.65
137.20
135.22
133.56
131.44
130.32
129.68
128.94
128.83
128.81
128.59
128.25
128.08
100.80
77.32
77.00
76.68
53.33
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

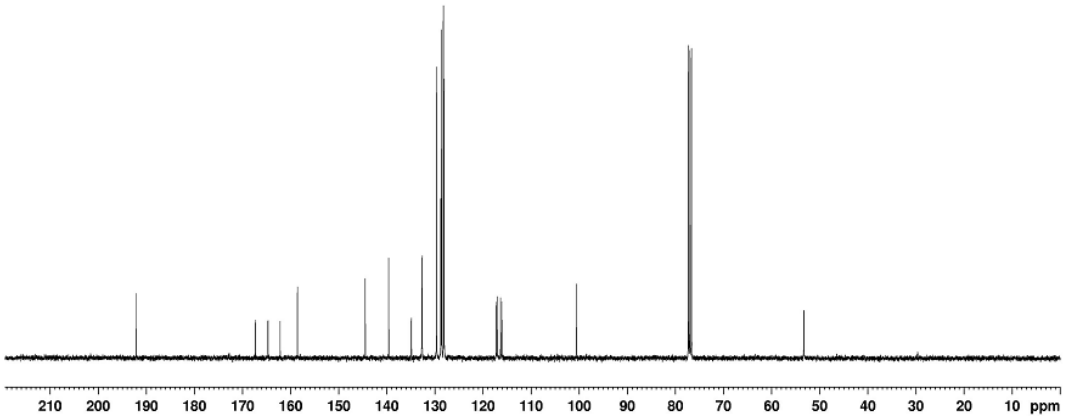

O
OMe
O
Ph
Ph
I
F

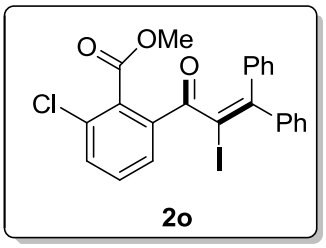
2n



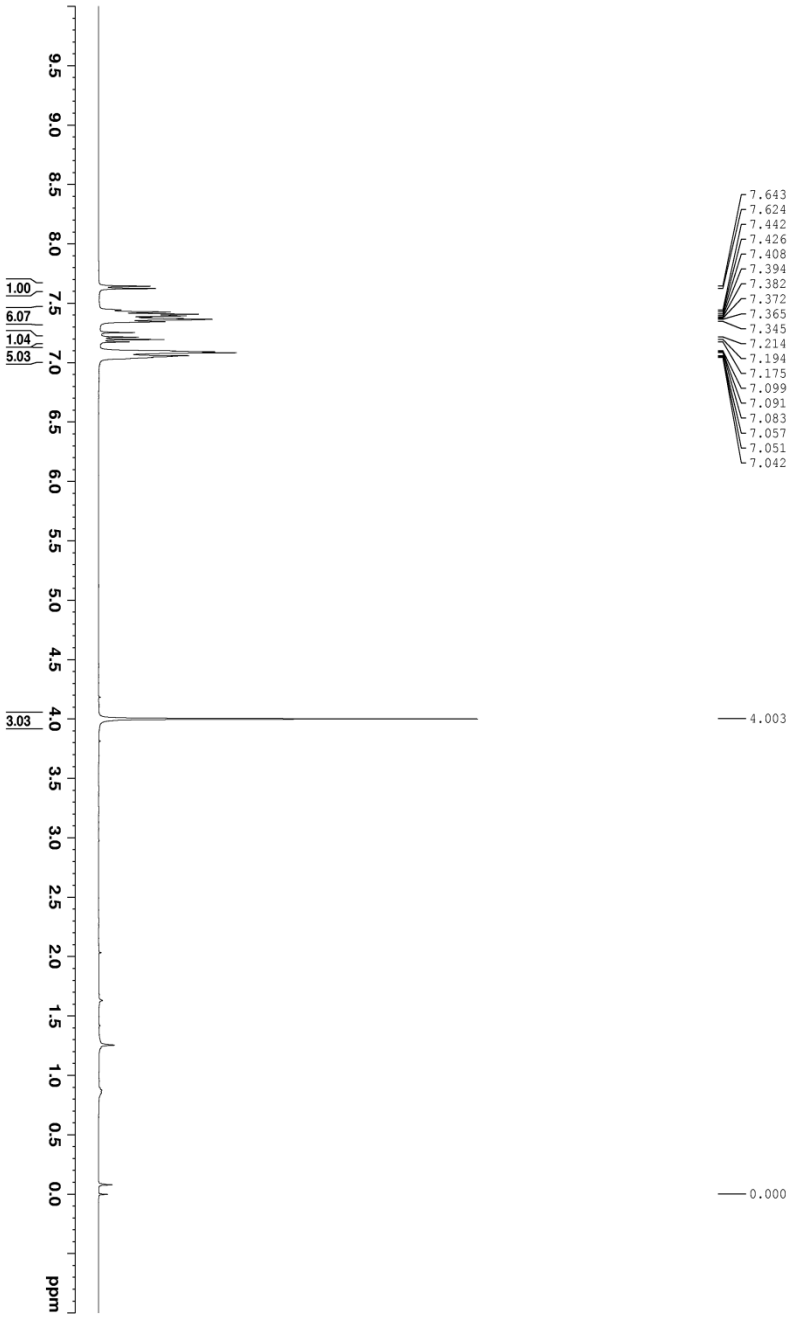

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.02
3.07
2.00
1.11
2.95
1.99
1.04
3.00

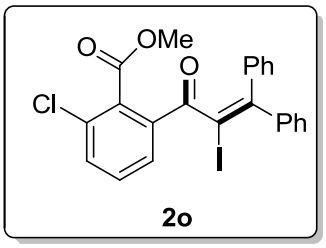



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

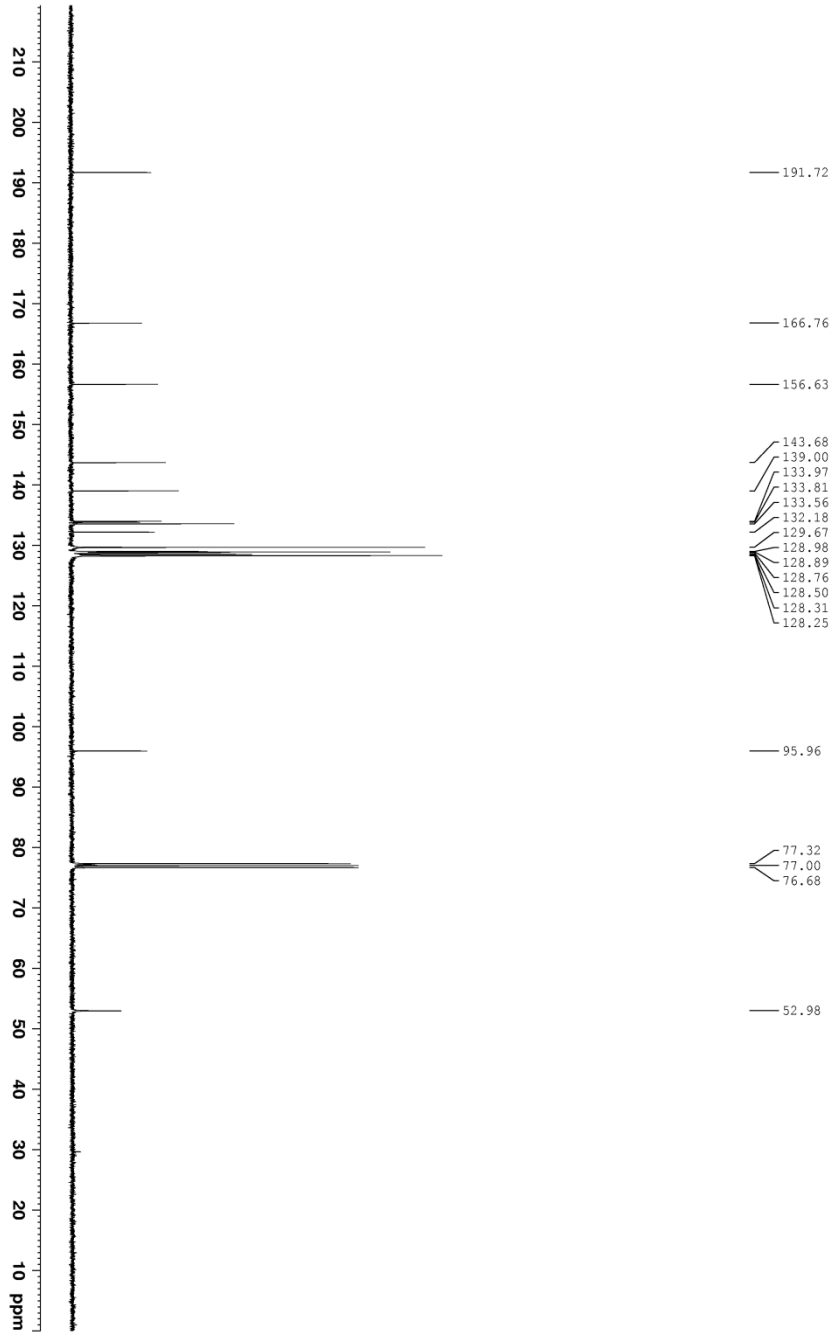

O
OMe
O
Ph
Cl
Ph
I

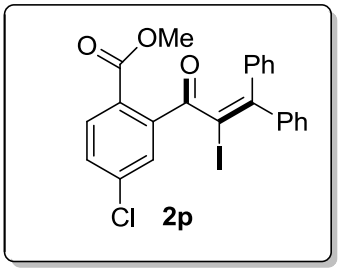
2o

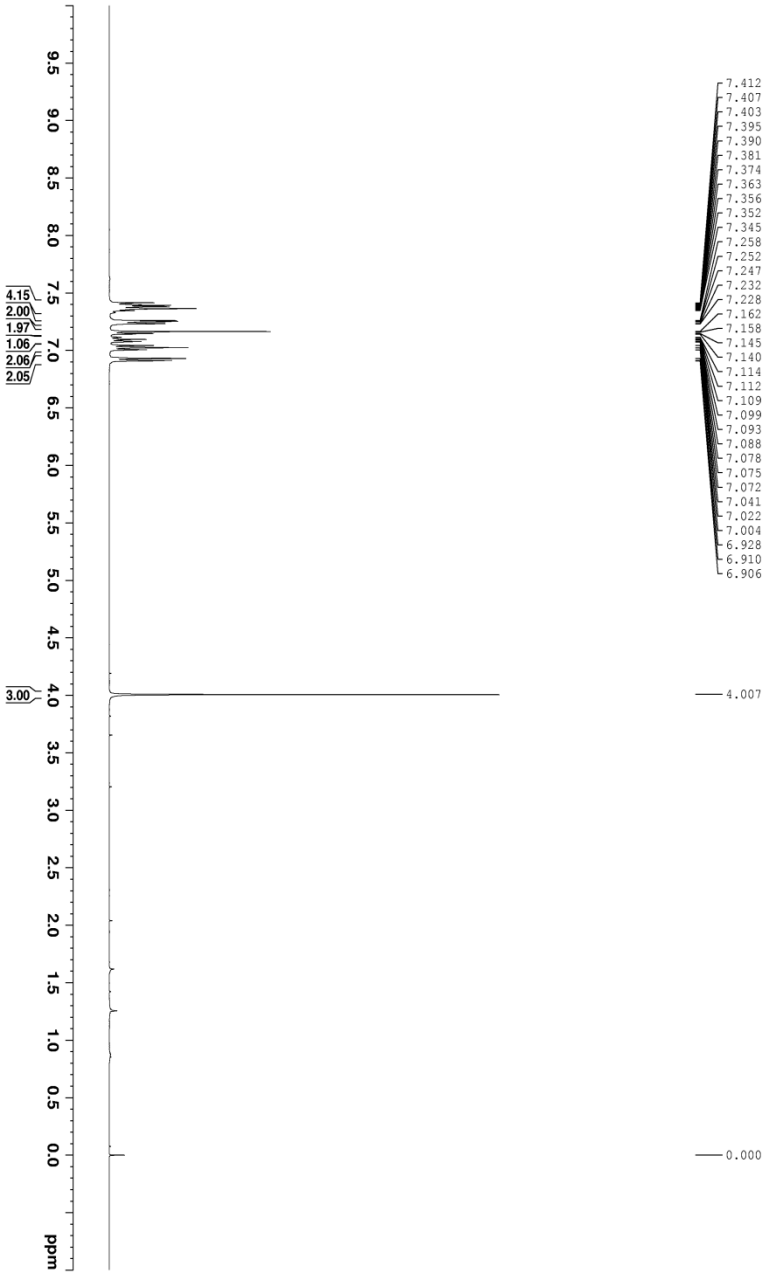

1.00
6.07
1.04
5.03
3.03
ppm
7.643
7.624
7.442
7.426
7.408
7.394
7.382
7.372
7.365
7.345
7.214
7.194
7.175
7.099
7.091
7.083
7.057
7.051
7.042
4.003
0.000

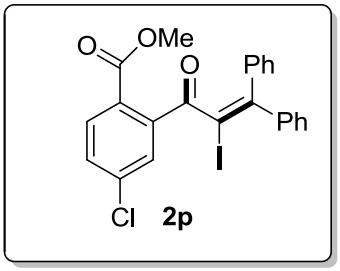

O
OMe
O
Ph
Cl
Ph
I

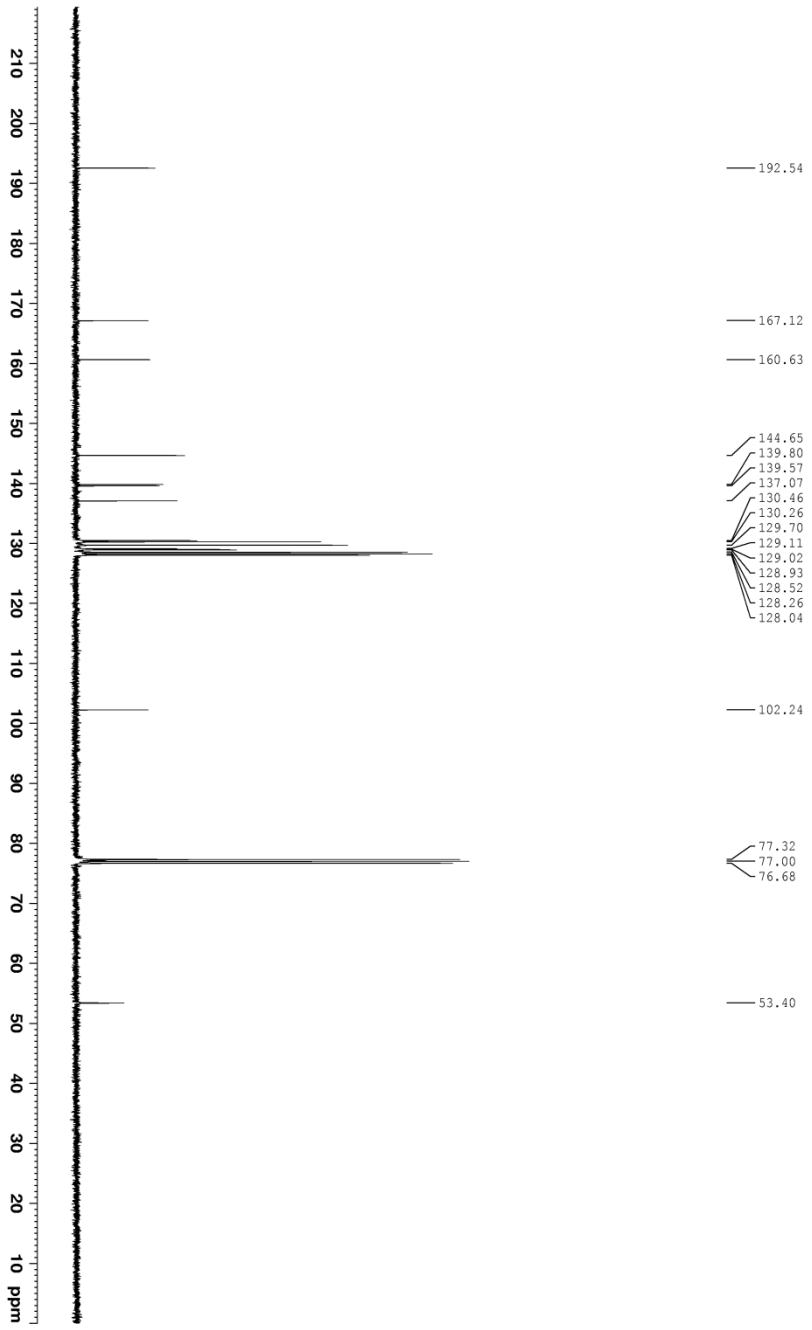
2o

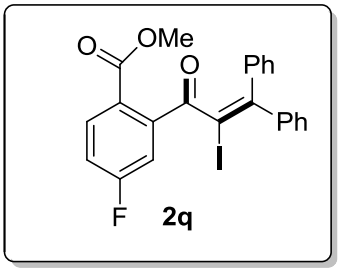

191.72
166.76
156.63
143.68
139.00
133.97
133.81
133.56
132.18
129.67
128.98
128.89
128.76
128.50
128.31
128.25
95.96
77.32
77.00
76.68
52.98
ppm

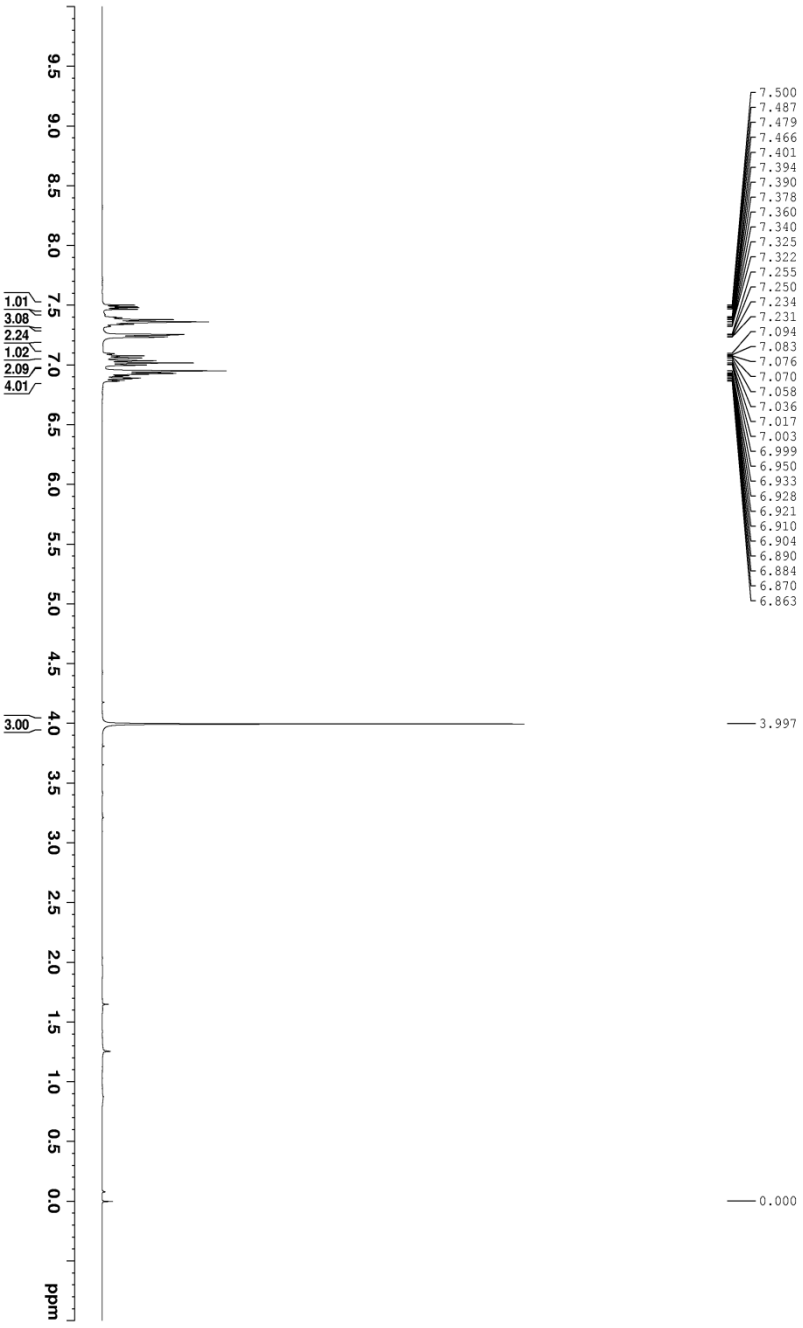

O
OMe
O
Ph
Ph
I
Cl
2p

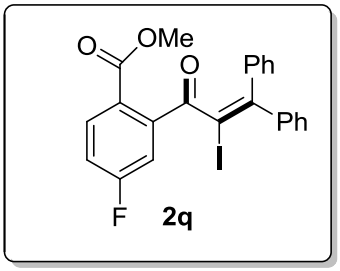

4.15
2.00
1.97
1.06
2.06
2.05
3.00
ppm
7.412
7.407
7.403
7.395
7.390
7.381
7.374
7.363
7.356
7.352
7.345
7.258
7.252
7.247
7.232
7.228
7.162
7.158
7.145
7.140
7.114
7.112
7.109
7.099
7.093
7.088
7.078
7.075
7.072
7.041
7.022
7.004
6.928
6.910
6.906
4.007
0.000

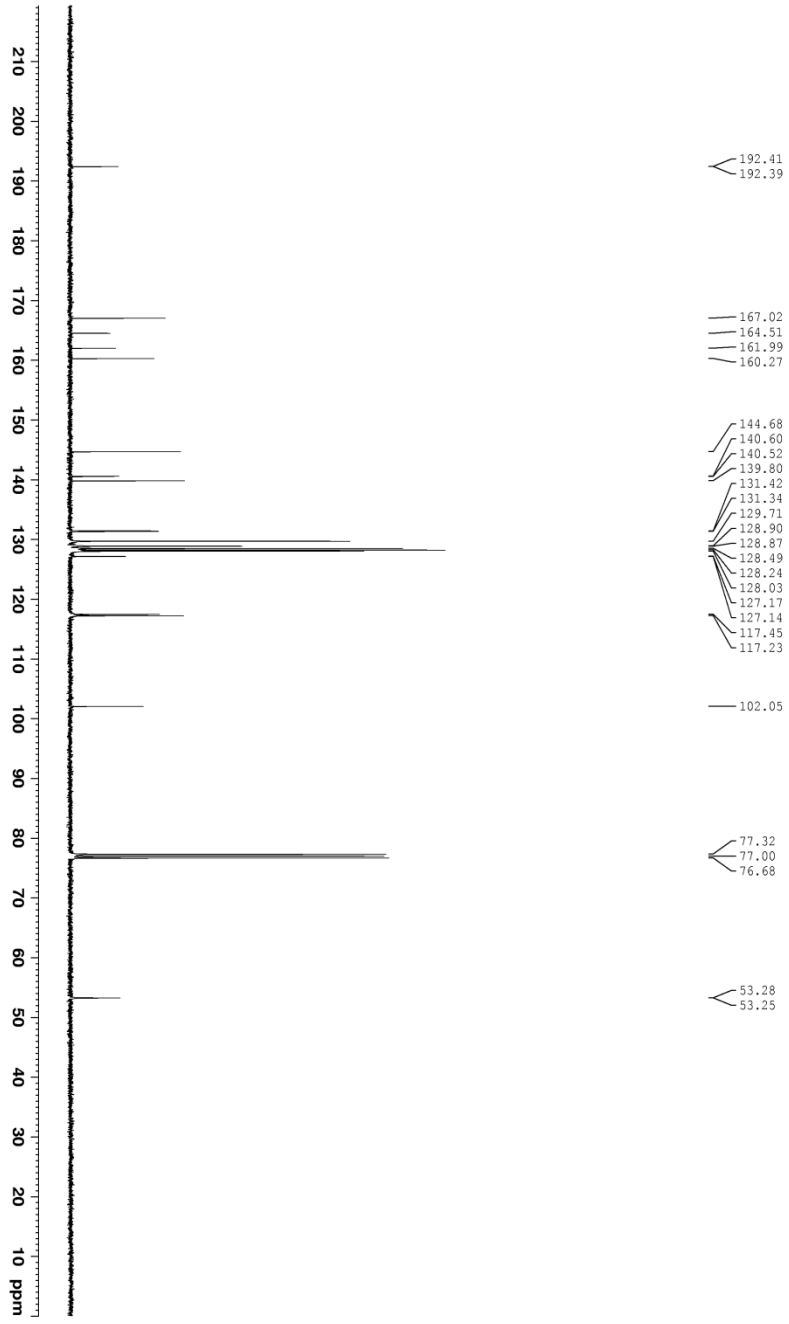

O
OMe
O
Ph
Ph
I
Cl
2p

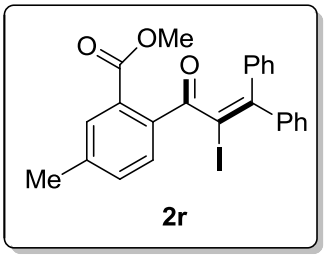

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
192.54
167.12
160.63
144.65
139.80
139.57
137.07
130.46
130.26
129.70
129.11
129.02
128.93
128.52
128.26
128.04
102.24
77.32
77.00
76.68
53.40


O
OMe
O
Ph
Ph
I
F
2q

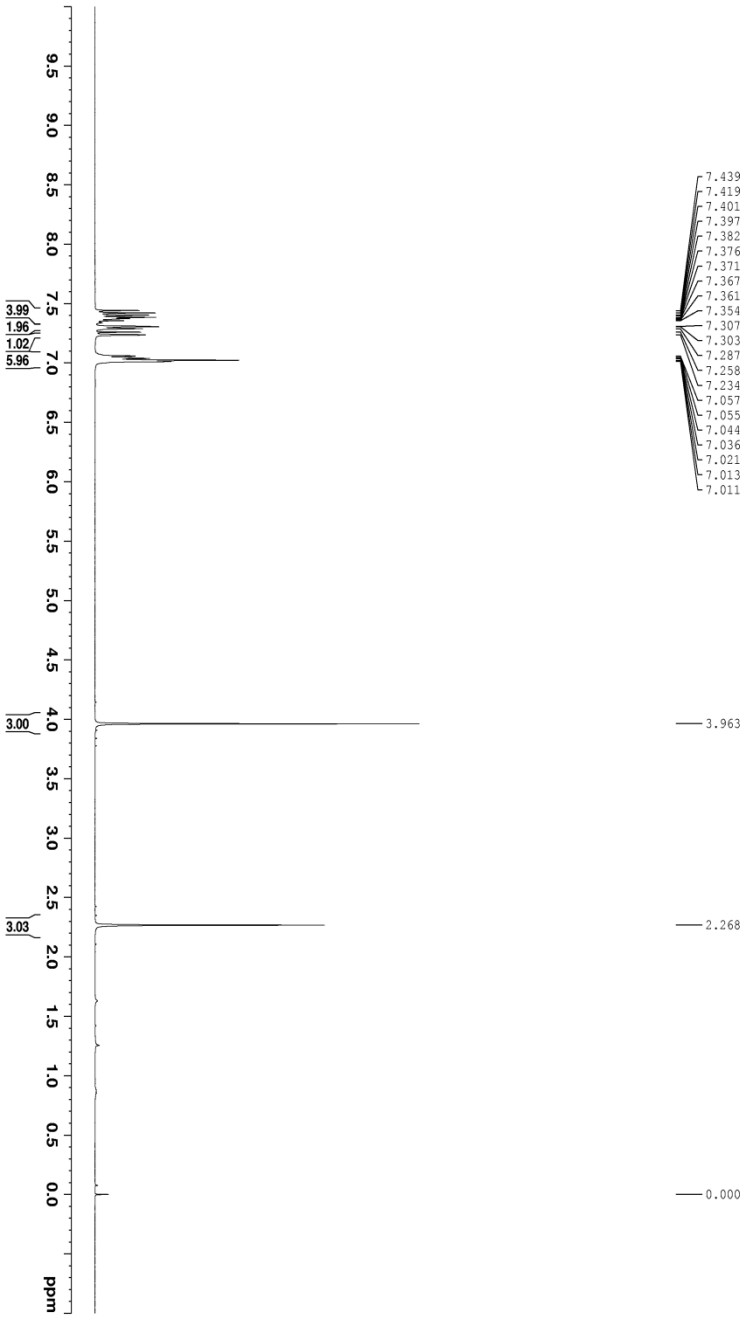

1.01
3.08
2.24
1.02
2.09
4.01
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
7.500
7.487
7.479
7.466
7.401
7.394
7.390
7.378
7.360
7.340
7.325
7.322
7.255
7.250
7.234
7.231
7.094
7.083
7.076
7.070
7.058
7.036
7.017
7.003
6.999
6.950
6.933
6.928
6.921
6.910
6.904
6.890
6.884
6.870
6.863
3.997
0.000

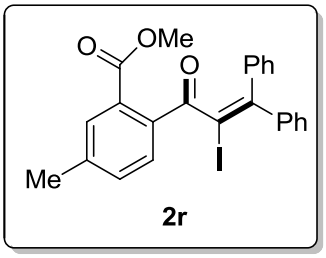

O
OMe
O
Ph
Ph
I
F
2q


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
192.41
192.39
167.02
164.51
161.99
160.27
144.68
140.60
140.52
139.80
131.42
131.34
129.71
128.90
128.87
128.49
128.24
128.03
127.17
127.14
117.45
117.23
102.05
77.32
77.00
76.68
53.28
53.25

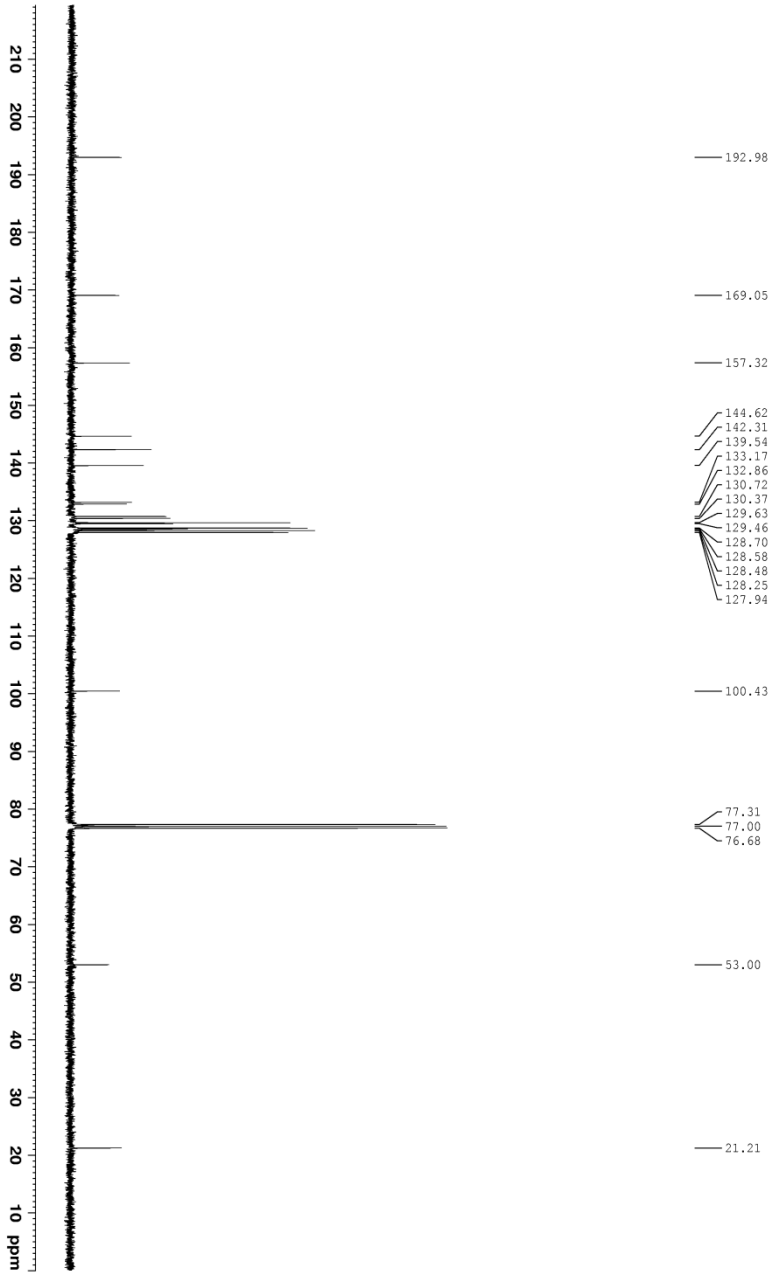

O
OMe
O
Ph
Ph
Me
I

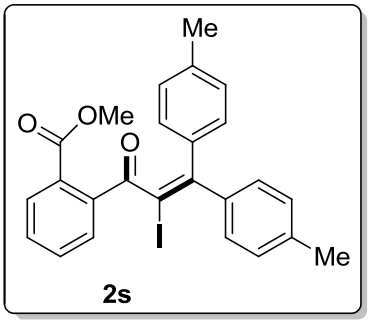
2r


3.99
1.96
1.02
5.96
3.00
3.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
7.439
7.419
7.401
7.397
7.382
7.376
7.371
7.367
7.361
7.354
7.307
7.303
7.287
7.258
7.234
7.057
7.055
7.044
7.036
7.021
7.013
7.011
3.963
2.268
0.000

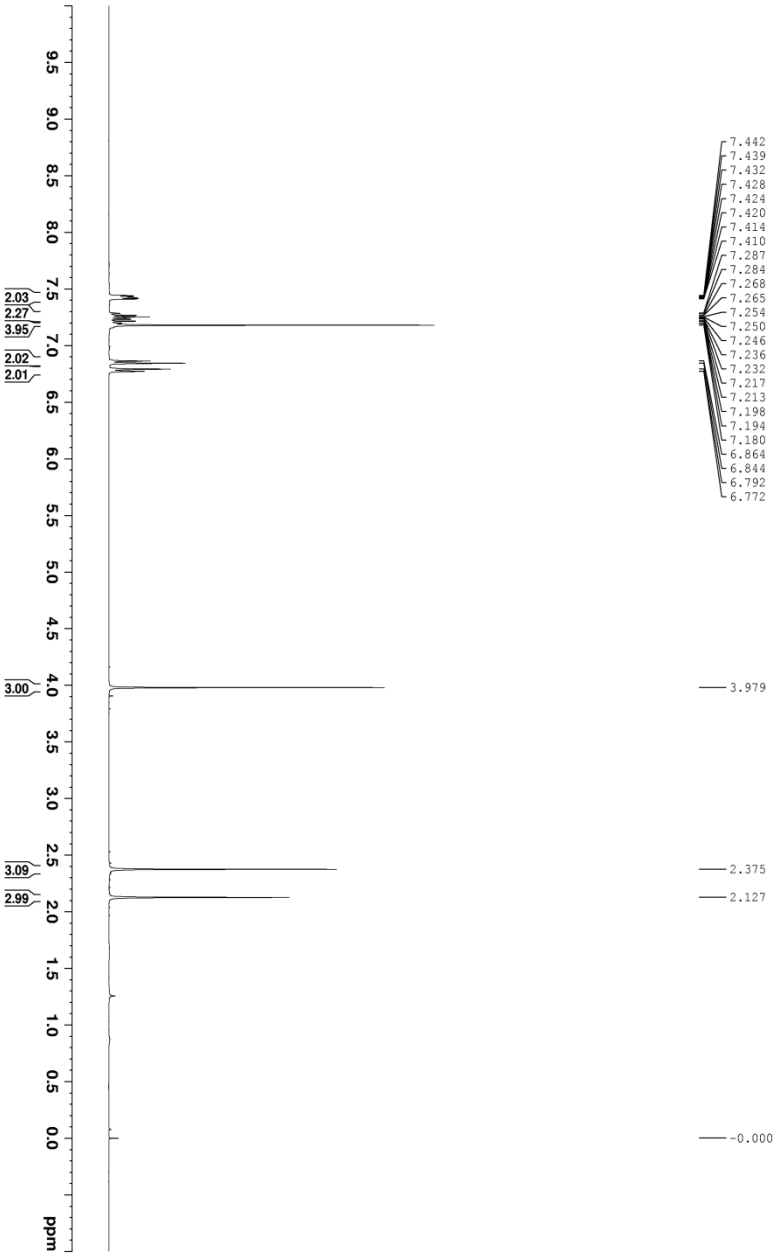

O
OMe
O
Ph
Ph
Me
I

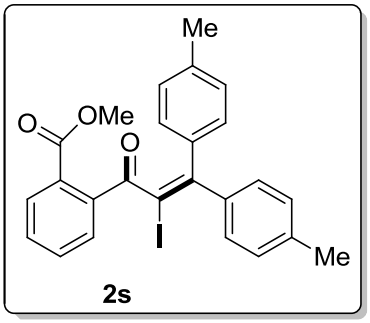
2r


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
192.98
169.05
157.32
144.62
142.31
139.54
133.17
132.86
130.72
130.37
129.63
129.46
128.70
128.58
128.48
128.25
127.94
100.43
77.31
77.00
76.68
53.00
21.21

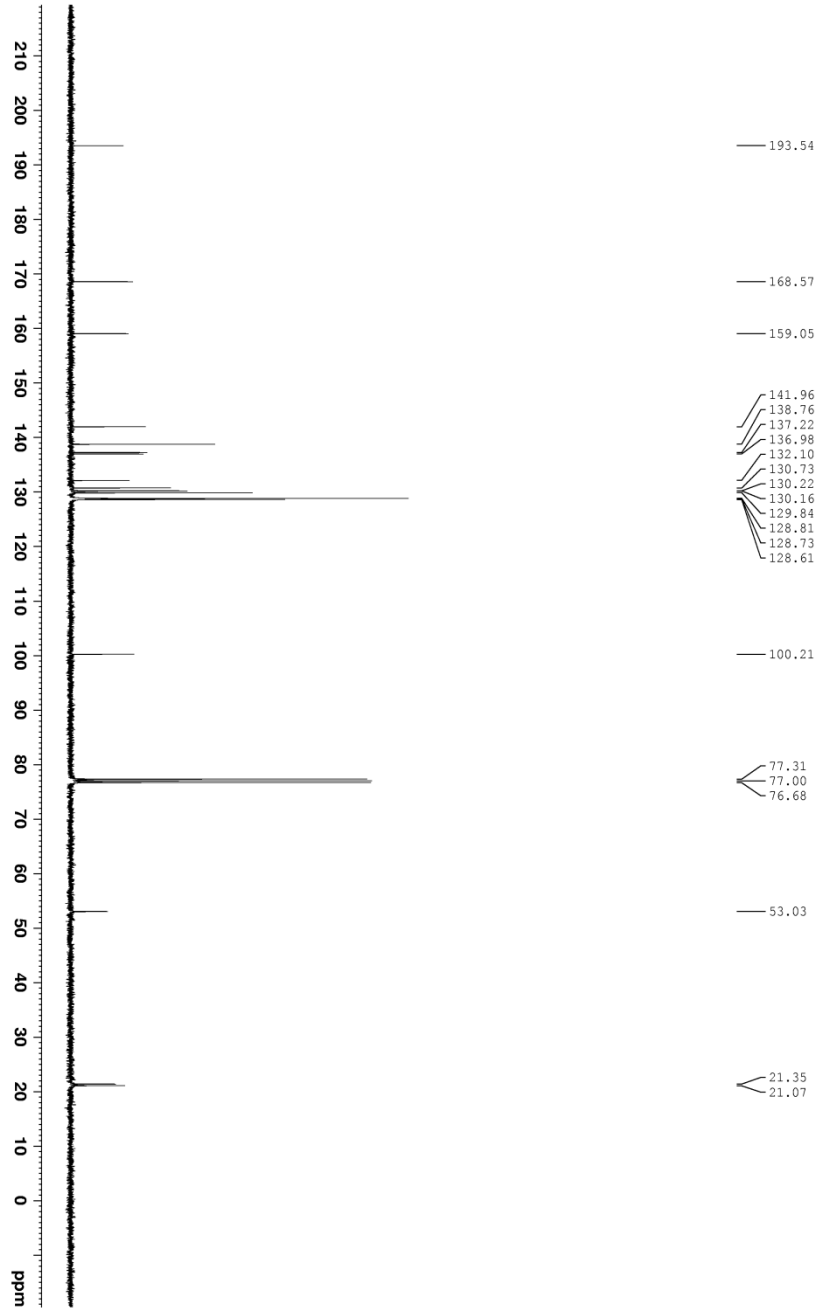

Me
OMe
O
O
I
Me

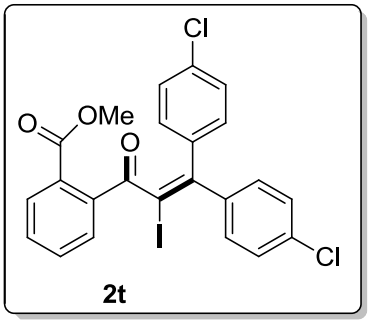
2s


9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.03
2.27
3.95
2.02
2.01
3.00
3.09
2.99
7.442
7.439
7.432
7.428
7.424
7.420
7.414
7.410
7.287
7.284
7.268
7.265
7.254
7.250
7.246
7.236
7.232
7.217
7.213
7.198
7.194
7.180
6.864
6.844
6.792
6.772
3.979
2.375
2.127
-0.000

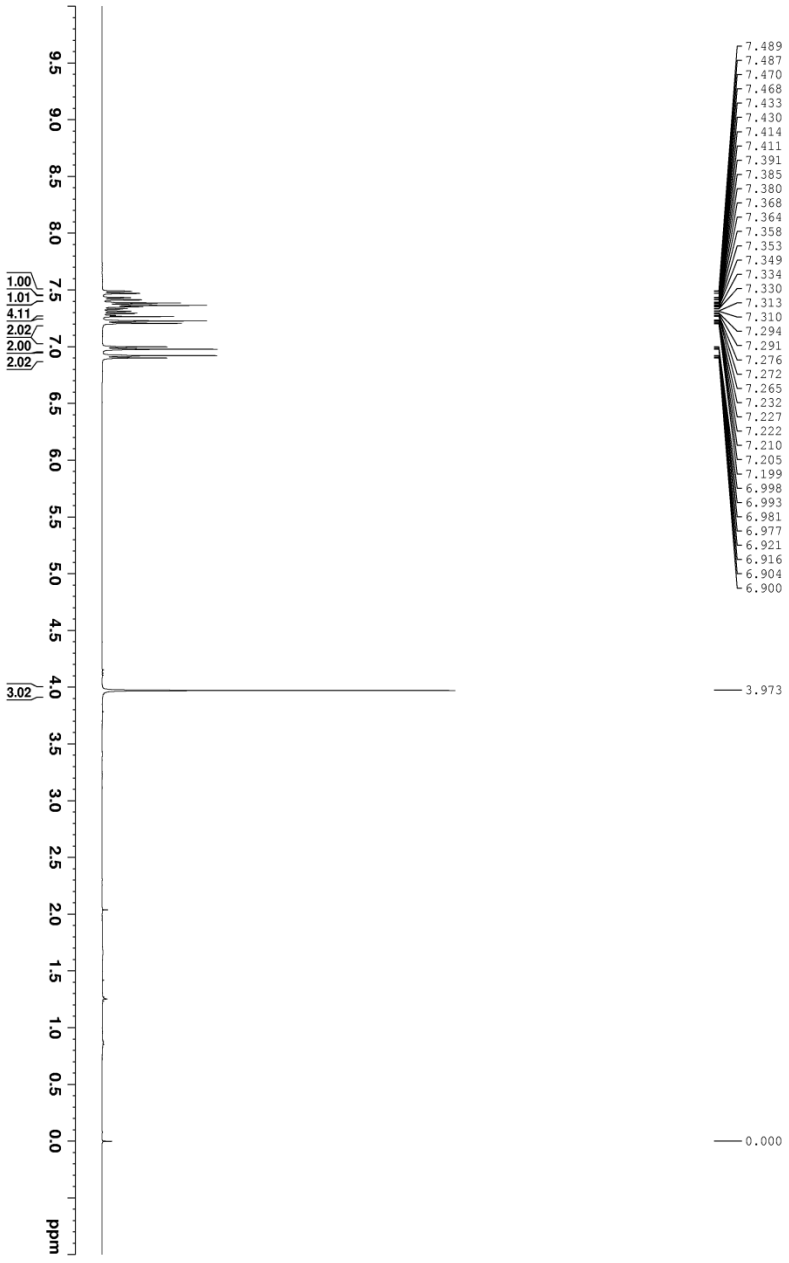

Me
OMe
O
O
I
Me

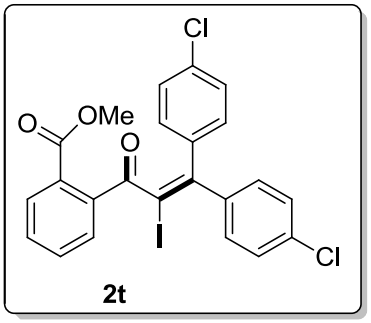
2s


193.54
168.57
159.05
141.96
138.76
137.22
136.98
132.10
130.73
130.22
130.16
129.84
128.81
128.73
128.61
100.21
77.31
77.00
76.68
53.03
21.35
21.07
ppm

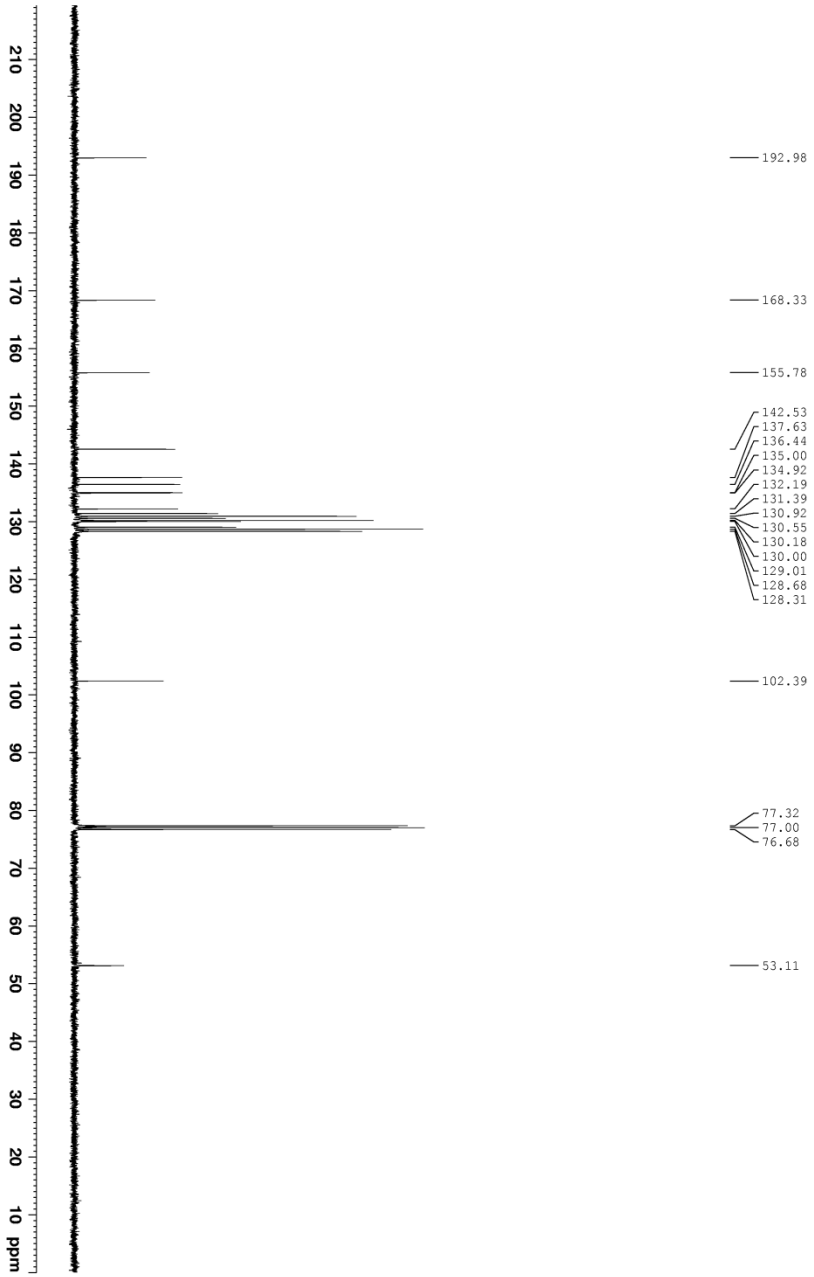

Cl
OMe
O
O
I
Cl

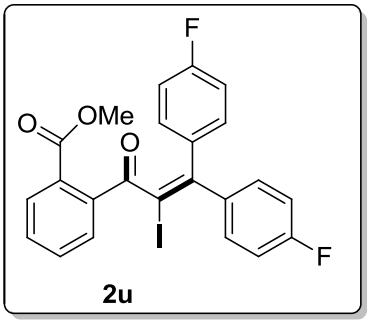
2t


1.00
1.01
4.11
2.02
2.00
2.02
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
7.489
7.487
7.470
7.468
7.433
7.430
7.414
7.411
7.391
7.385
7.380
7.368
7.364
7.358
7.353
7.349
7.334
7.330
7.313
7.310
7.294
7.291
7.276
7.272
7.265
7.232
7.227
7.222
7.210
7.205
7.199
6.998
6.993
6.981
6.977
6.921
6.916
6.904
6.900
3.973
0.000

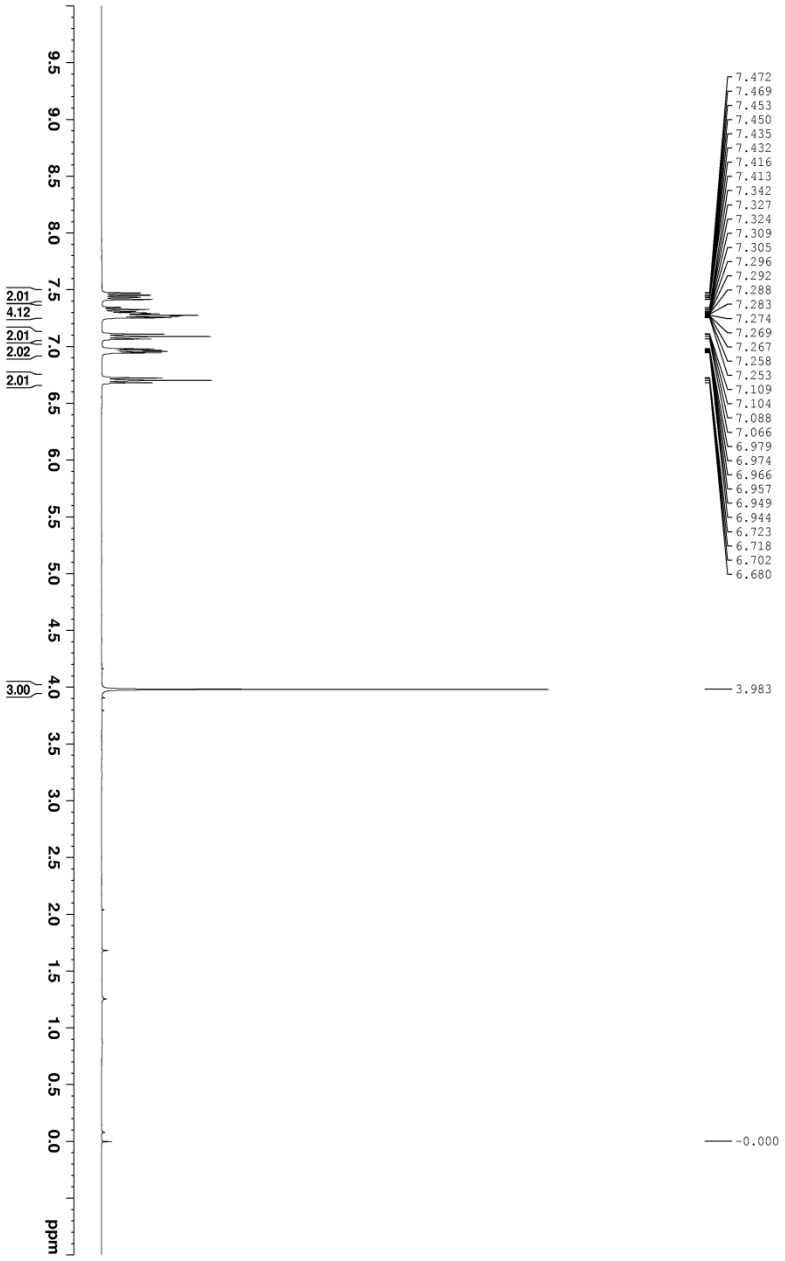

Cl
O
OMe
O
I
Cl

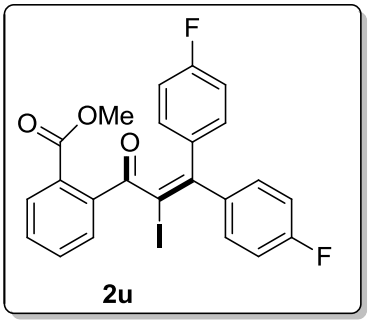
2t


192.98
168.33
155.78
142.53
137.63
136.44
135.00
134.92
132.19
131.39
130.92
130.55
130.18
130.00
129.01
128.68
128.31
102.39
77.32
77.00
76.68
53.11
ppm

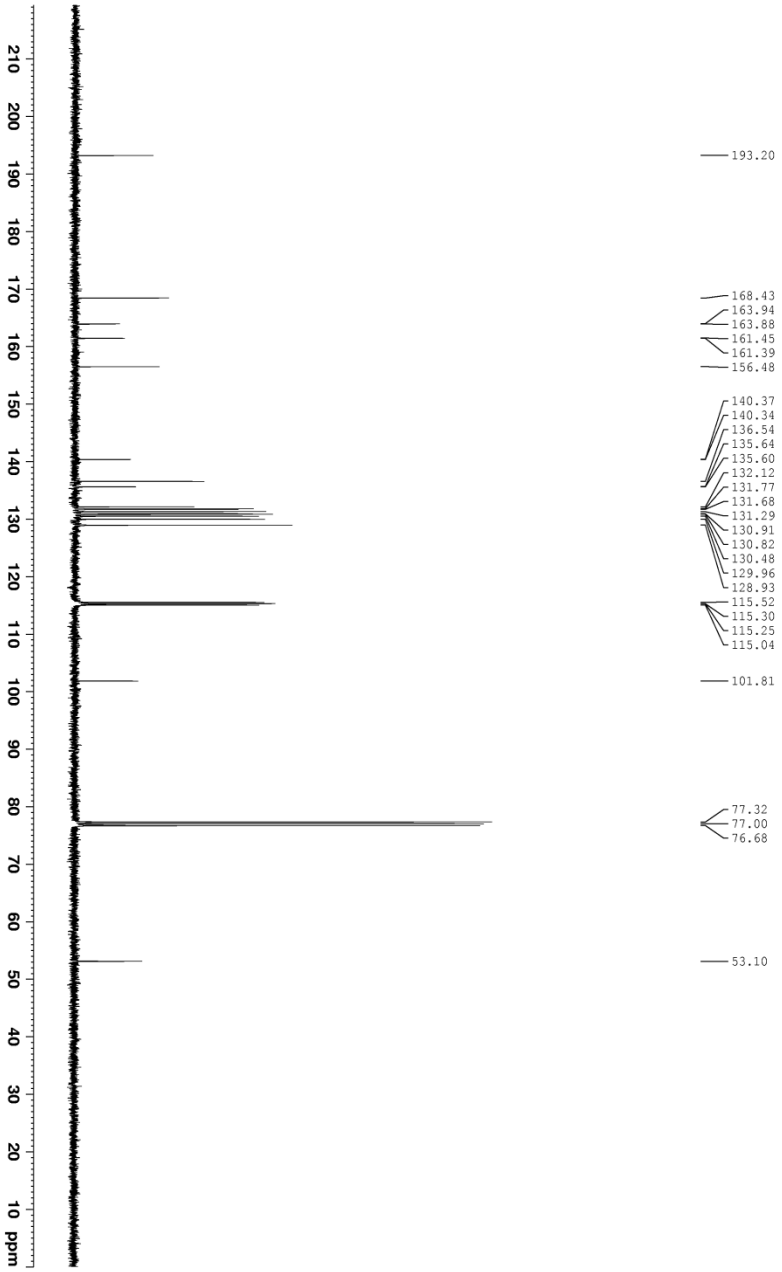

F
O
OMe
O
I
F

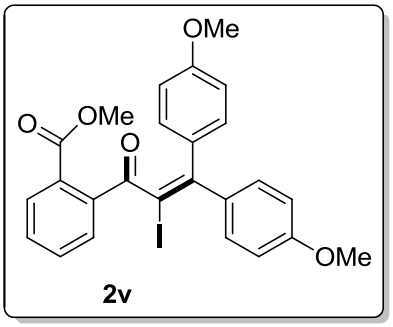
2u


2.01
4.12
2.01
2.02
2.01
3.00
7.472
7.469
7.453
7.450
7.435
7.432
7.416
7.413
7.342
7.327
7.324
7.309
7.305
7.296
7.292
7.288
7.283
7.274
7.269
7.267
7.258
7.253
7.109
7.104
7.088
7.066
6.979
6.974
6.966
6.957
6.949
6.944
6.723
6.718
6.702
6.680
3.983
-0.000
ppm

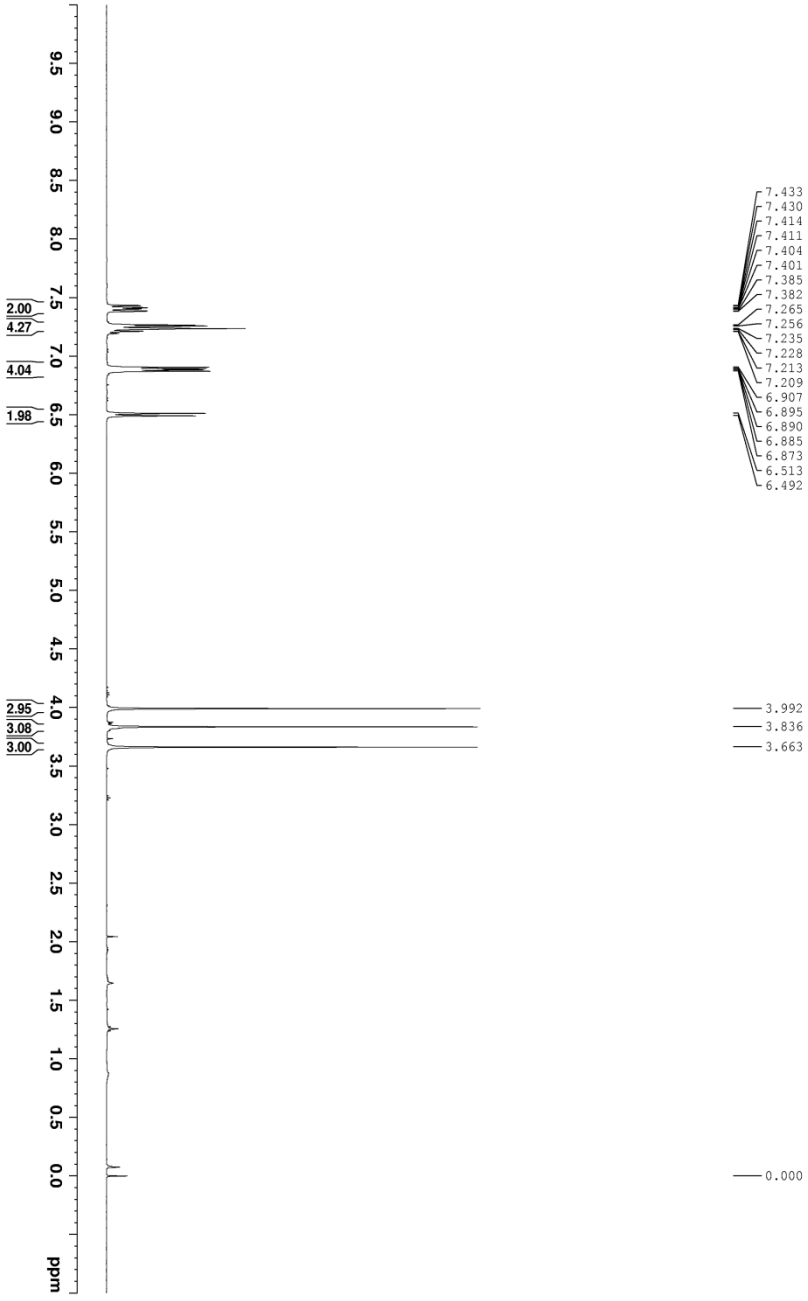

F
O
OMe
O
I
F

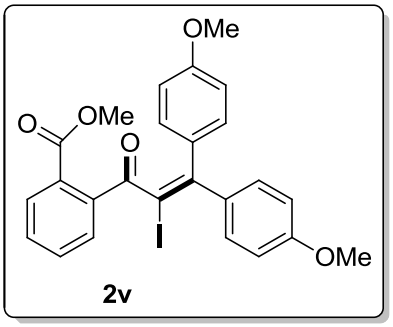
2u


193.20
168.43
163.94
163.88
161.45
161.39
156.48
140.37
140.34
136.54
135.64
135.60
132.12
131.77
131.68
131.29
130.91
130.82
130.48
129.96
128.93
115.52
115.30
115.25
115.04
101.81
77.32
77.00
76.68
53.10
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

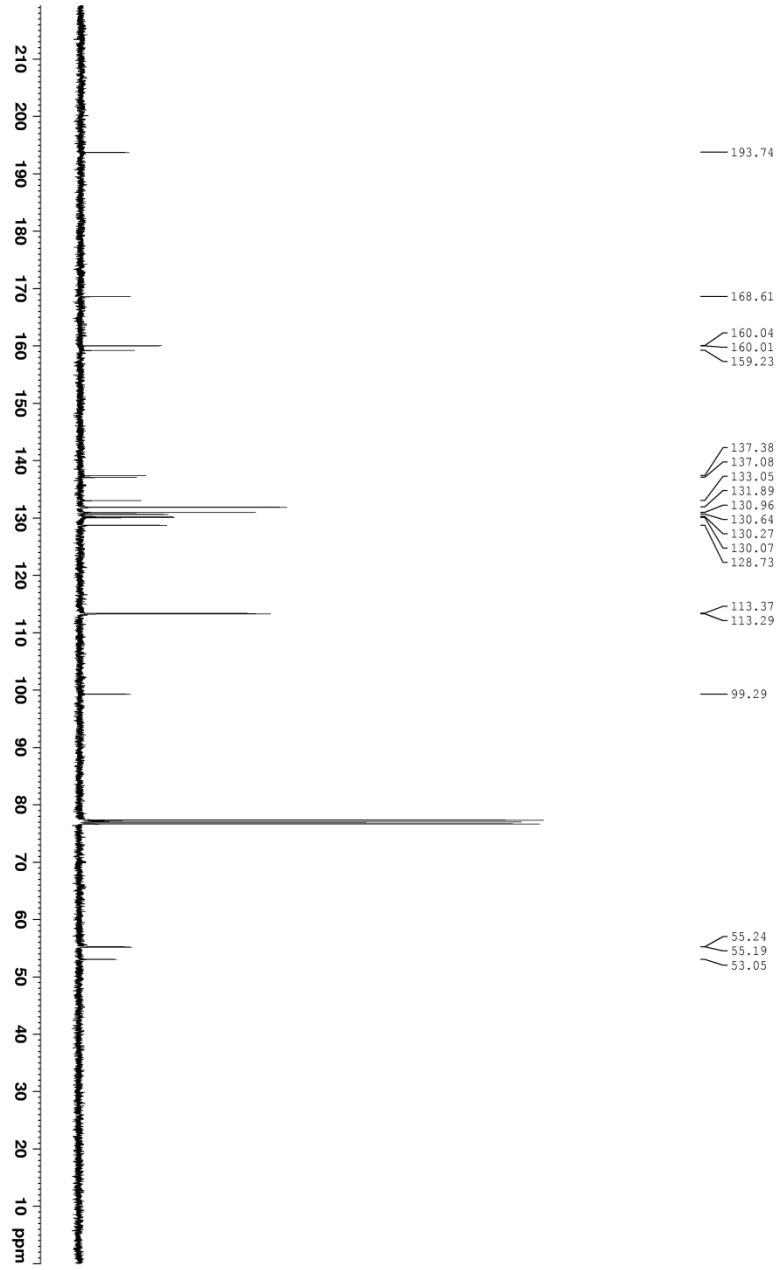

OMe
O
OMe
O
I
OMe

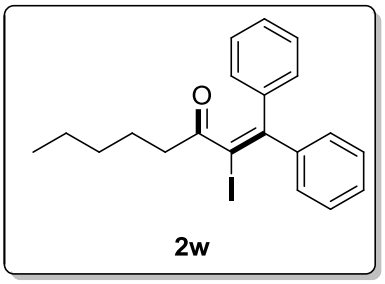
2v


2.00
4.27
4.04
1.98
2.95
3.08
3.00
7.433
7.430
7.414
7.411
7.404
7.401
7.385
7.382
7.265
7.256
7.235
7.228
7.213
7.209
6.907
6.895
6.890
6.885
6.873
6.513
6.492
3.992
3.836
3.663
0.000
ppm

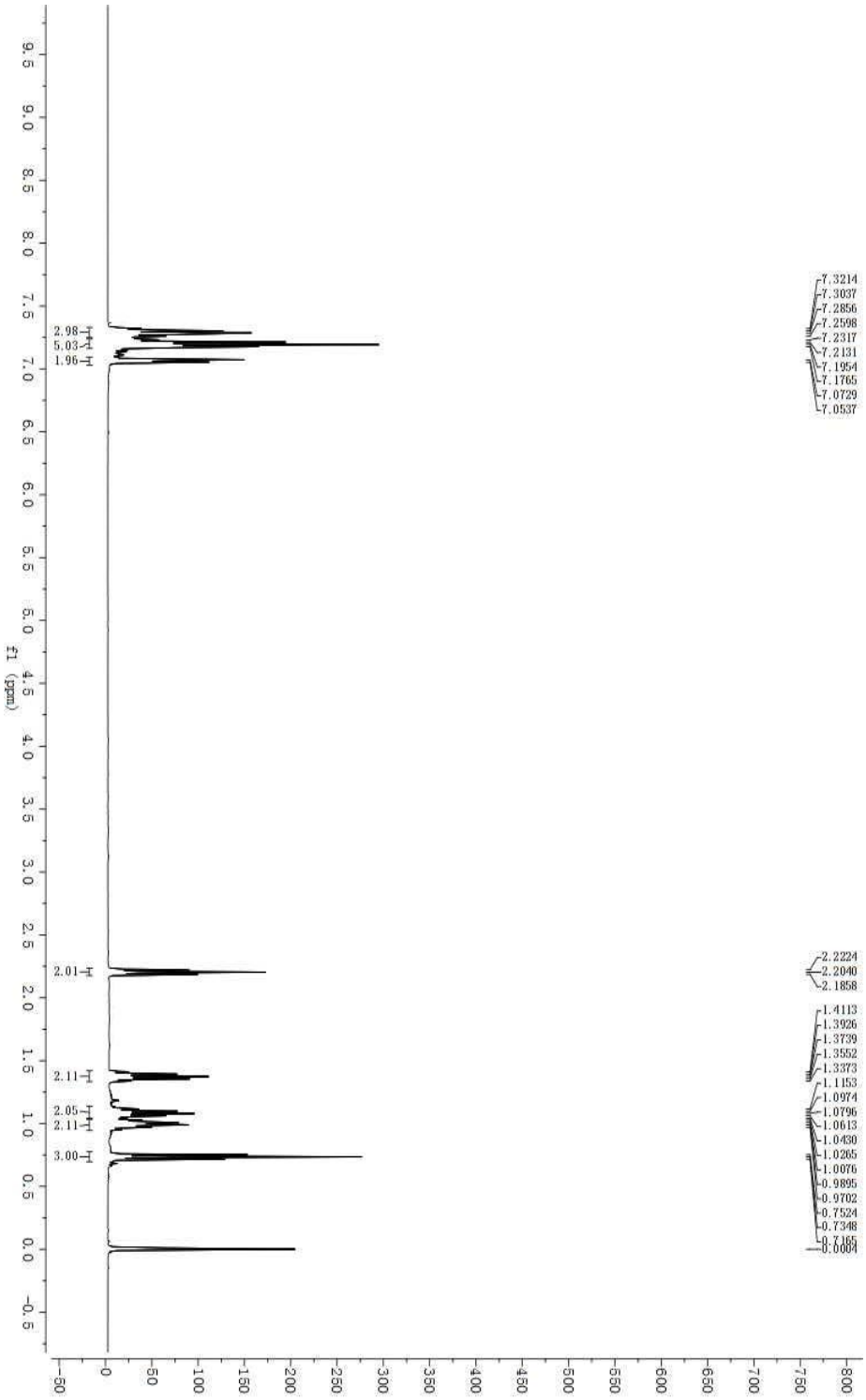

OMe
O
OMe
O
I
OMe

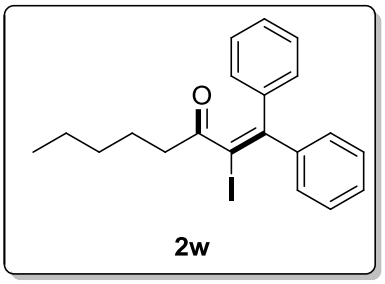
2v


193.74
168.61
160.04
160.01
159.23
137.38
137.08
133.05
131.89
130.96
130.64
130.27
130.07
128.73
113.37
113.29
99.29
55.24
55.19
53.05
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

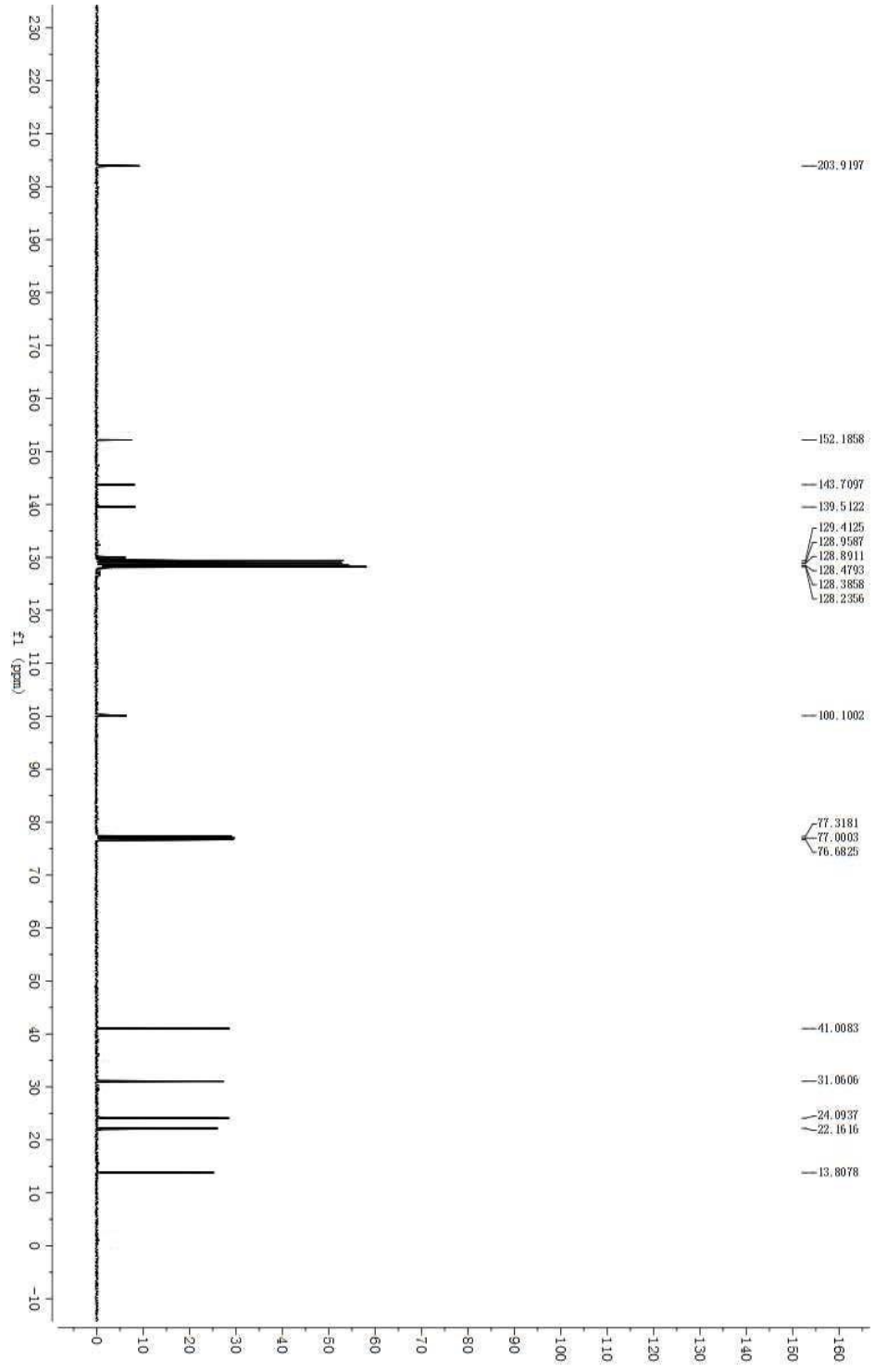

O
I

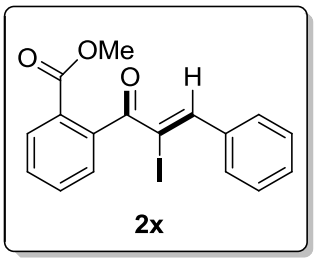
2w


f1 (ppm)
2.98
5.03
1.96
2.01
2.11
2.05
2.11
3.00
7.3214
7.3037
7.2856
7.2598
7.2317
7.2131
7.1954
7.1765
7.0729
7.0537
2.2224
2.2040
2.1858
1.4113
1.3926
1.3739
1.3552
1.3373
1.1153
1.0974
1.0796
1.0613
1.0430
1.0265
1.0076
0.9895
0.9702
0.7524
0.7348
0.7165
0.0004

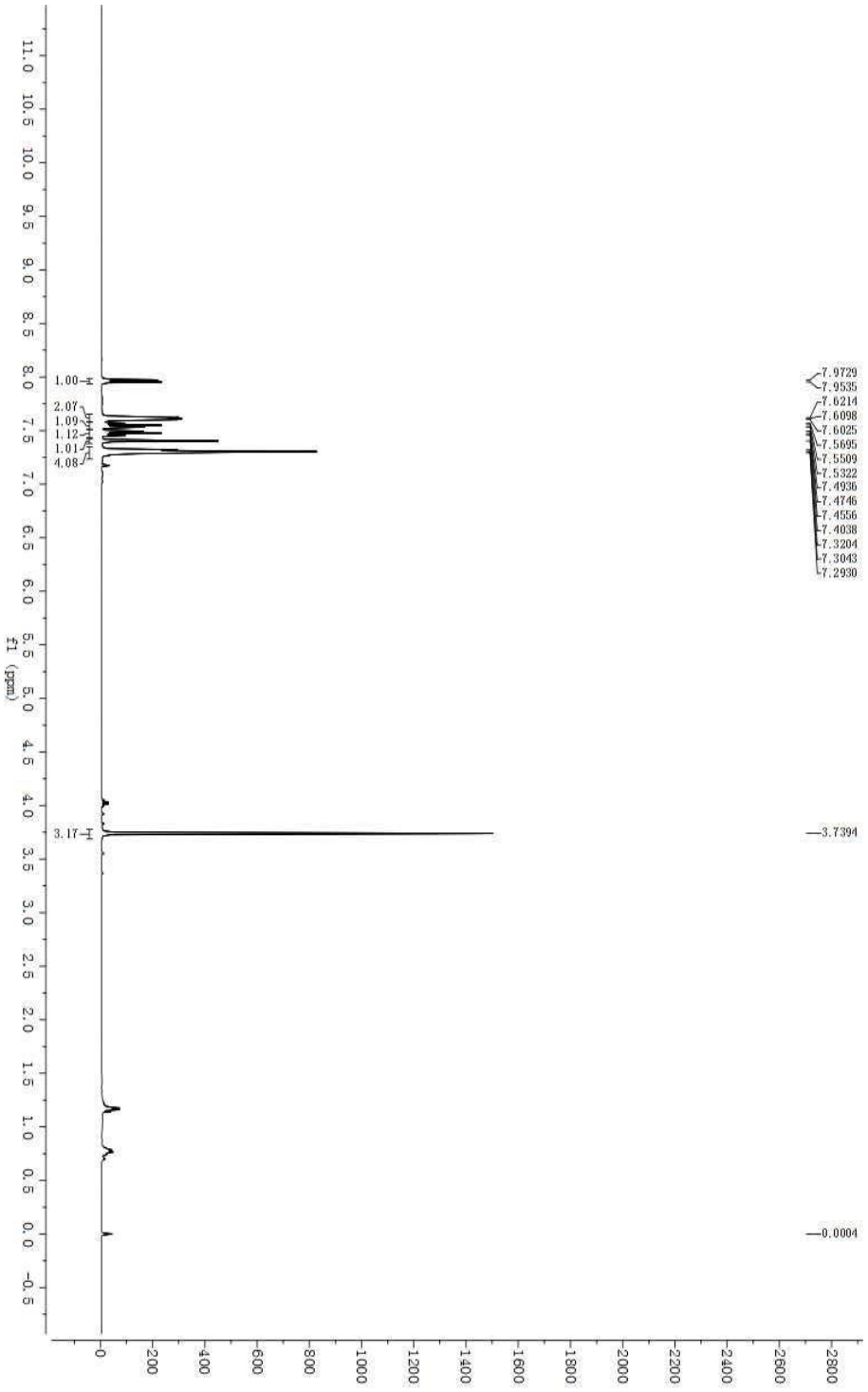

O
I

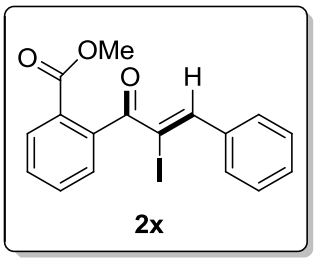
2w


f1 (ppm)
203.9197
152.1858
143.7097
139.5122
129.4125
128.9587
128.8911
128.4793
128.3858
128.2356
100.1002
77.3181
77.0003
76.6825
41.0083
31.0606
24.0937
22.1616
13.8078

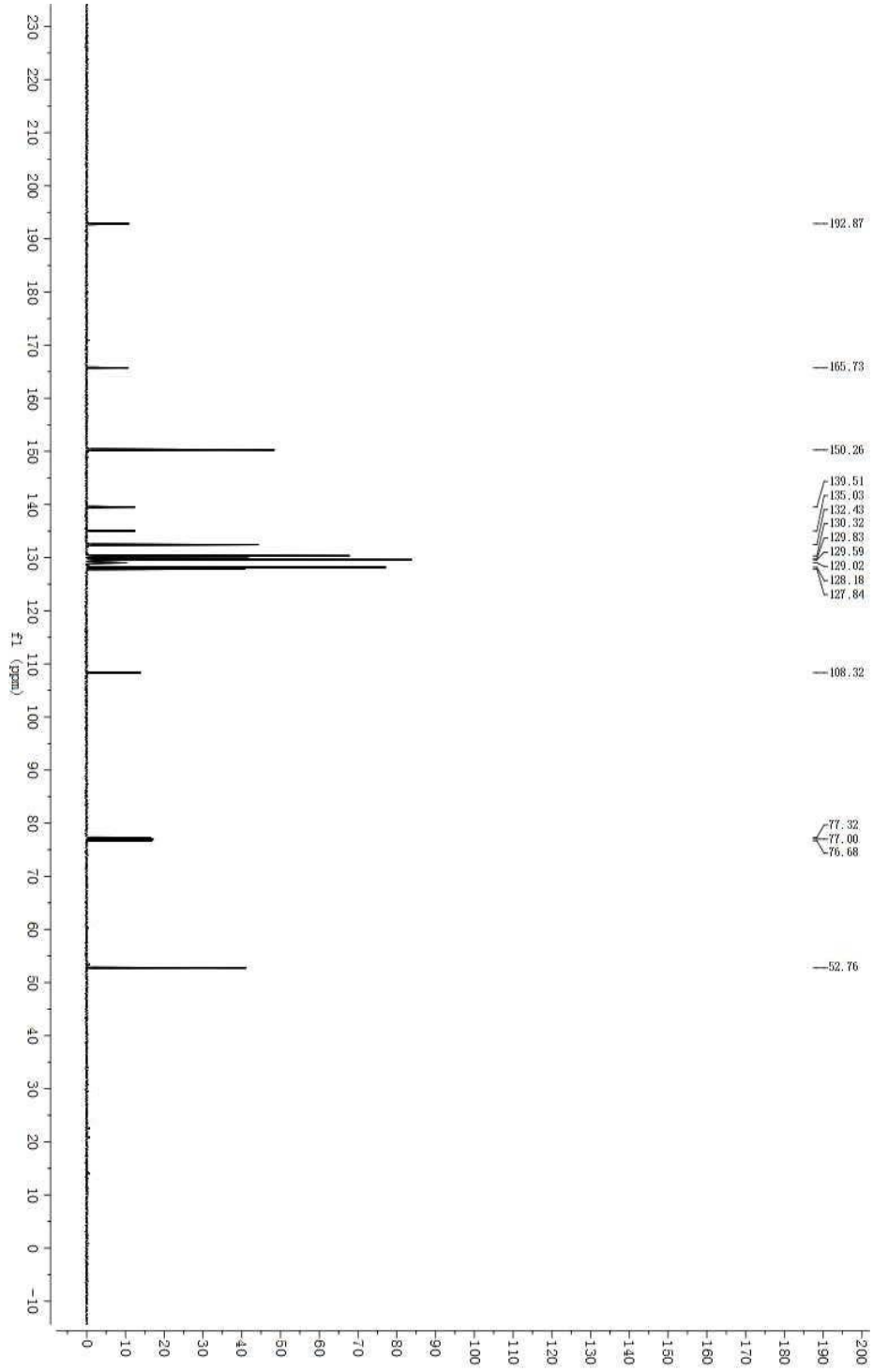

O
OMe
O
H
I

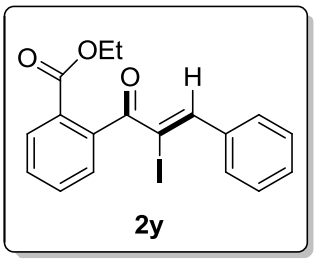
2x


f1 (ppm)
1.00
2.07
1.09
1.12
1.01
4.08
3.17
7.9729
7.9535
7.6214
7.6098
7.6025
7.5695
7.5509
7.5322
7.4936
7.4746
7.4556
7.4038
7.3204
7.3043
7.2930
3.7394
0.0004

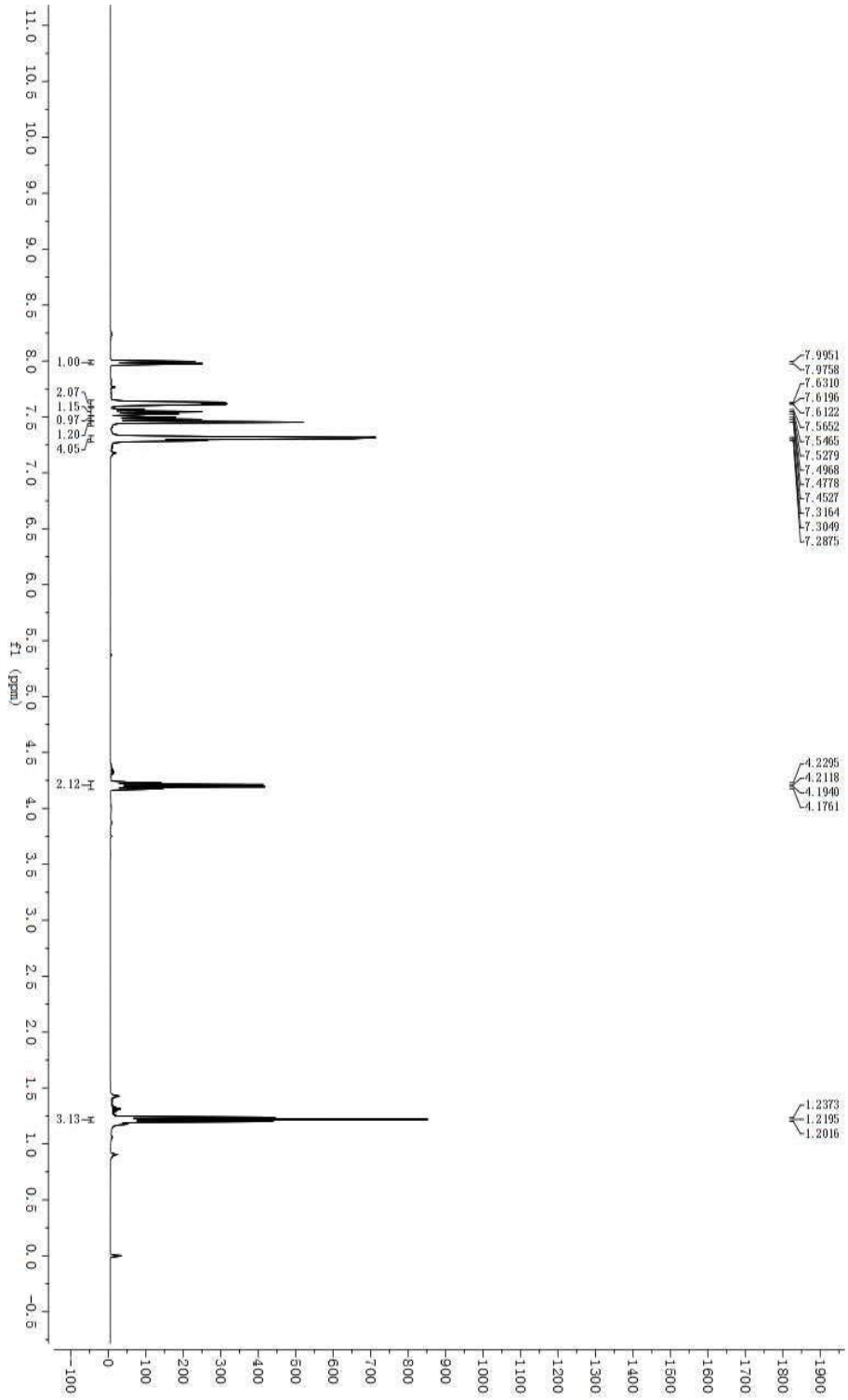

O
OMe
O
H
I

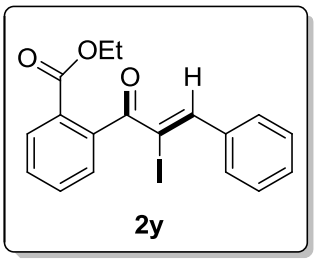
2x


192.87
165.73
150.26
139.51
135.03
132.43
130.32
129.83
129.59
129.02
128.18
127.84
108.32
77.32
77.00
76.68
52.76
f1 (ppm)

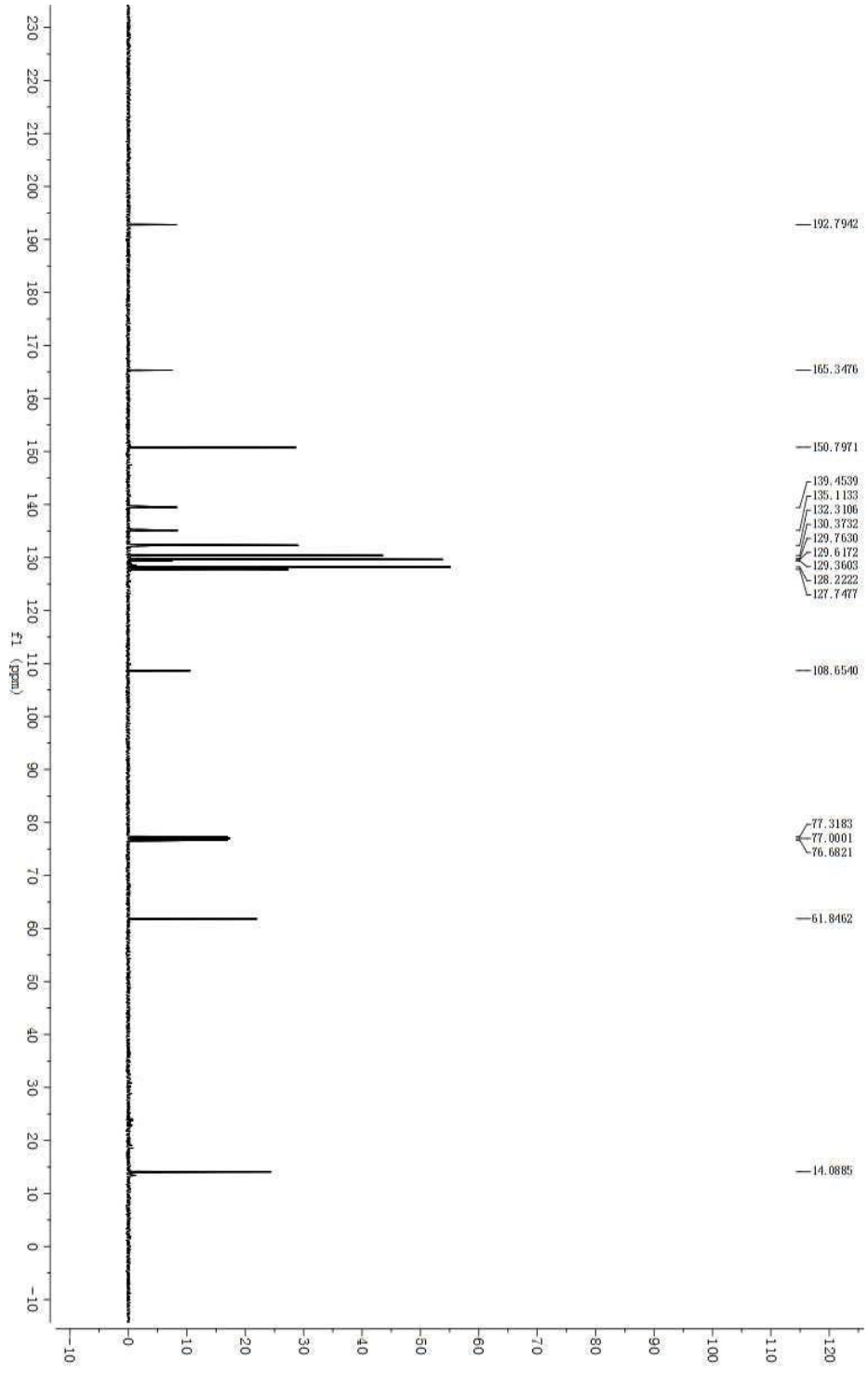

O
OEt
O
H
I

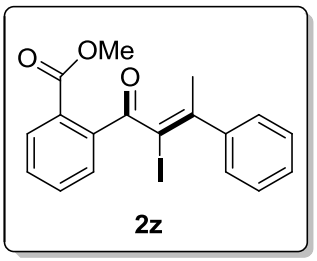
2y


1.00
2.07
1.15
0.97
1.20
4.05
2.12
3.13
7.9951
7.9758
7.6310
7.6196
7.6122
7.5652
7.5465
7.5279
7.4968
7.4778
7.4527
7.3164
7.3049
7.2875
4.2295
4.2118
4.1940
4.1761
1.2373
1.2195
1.2016
f1 (ppm)

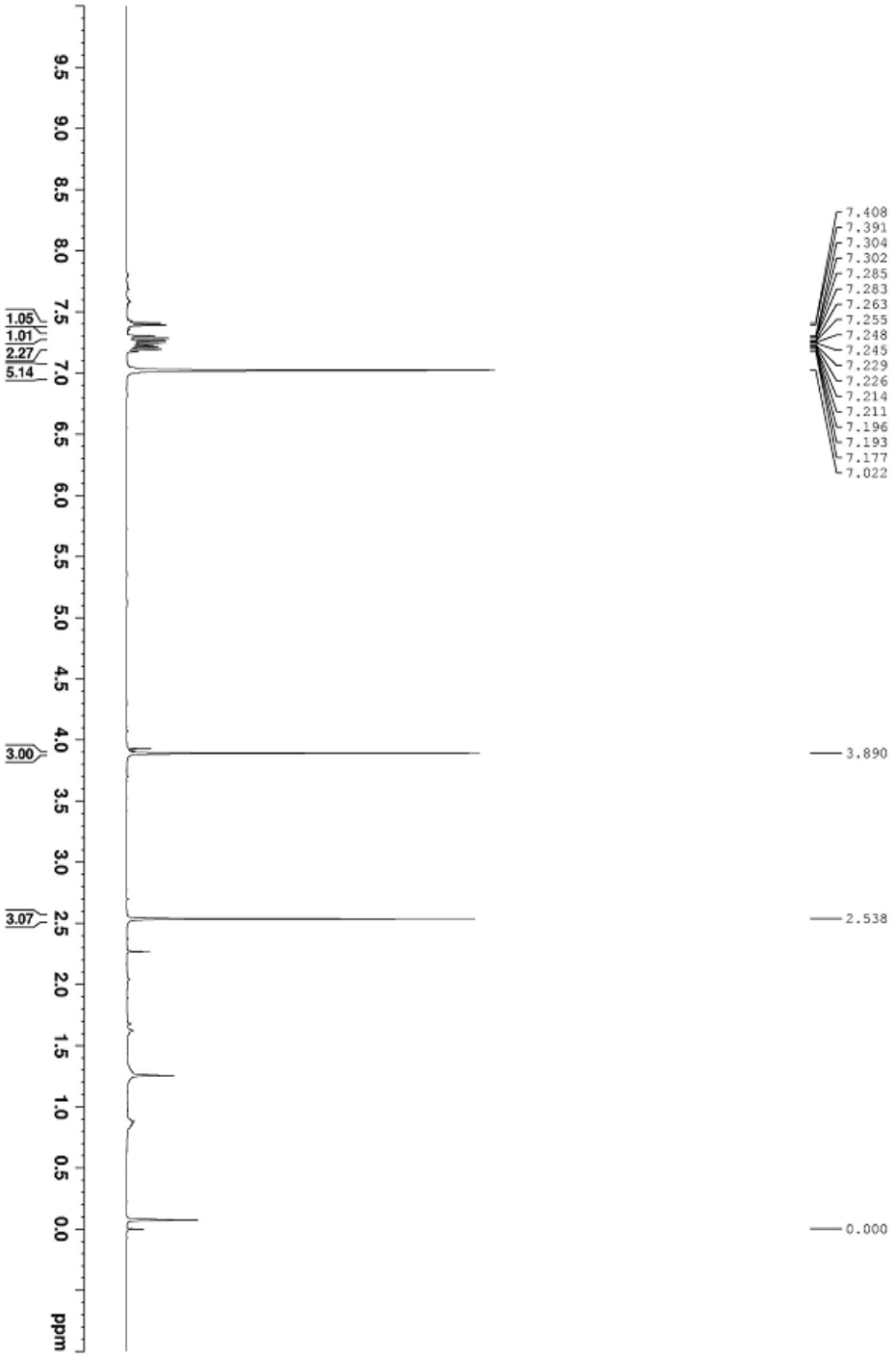

O
OEt
O
H
I

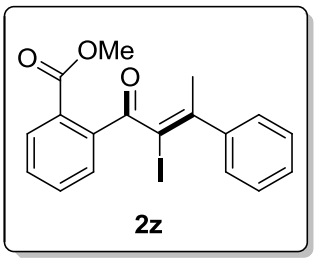
2y


192.7942
165.3476
150.7971
139.4539
135.1133
132.3106
130.3732
129.7630
129.6172
129.3603
128.2222
127.7477
108.6540
77.3183
77.0001
76.6821
61.8462
14.0885
f1 (ppm)

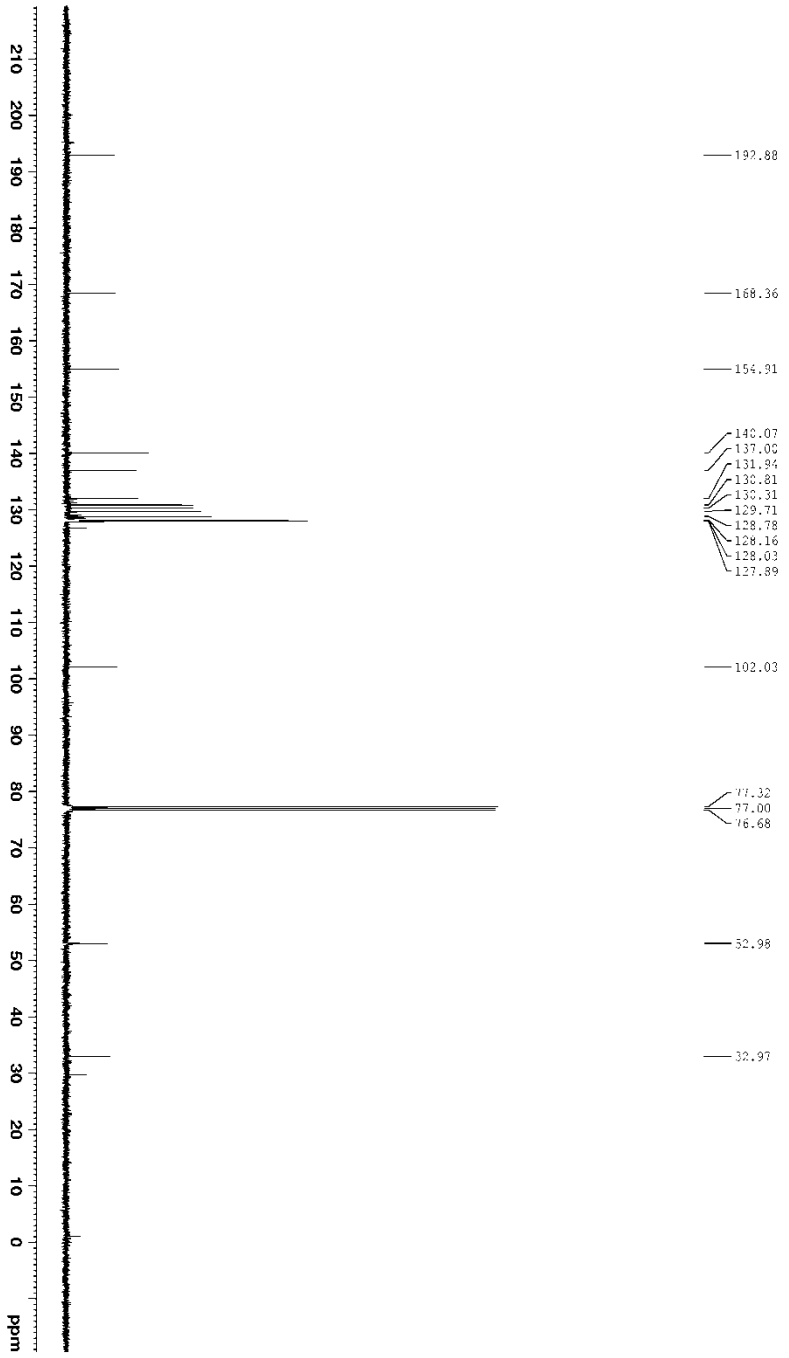

O
OMe
O
I

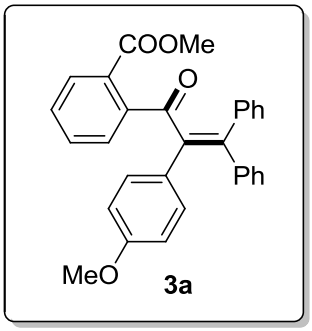
2z


1.05
1.01
2.27
5.14
3.00
3.07
ppm
7.408
7.391
7.304
7.302
7.285
7.283
7.263
7.255
7.248
7.245
7.229
7.226
7.214
7.211
7.196
7.193
7.177
7.022
3.890
2.538
0.000

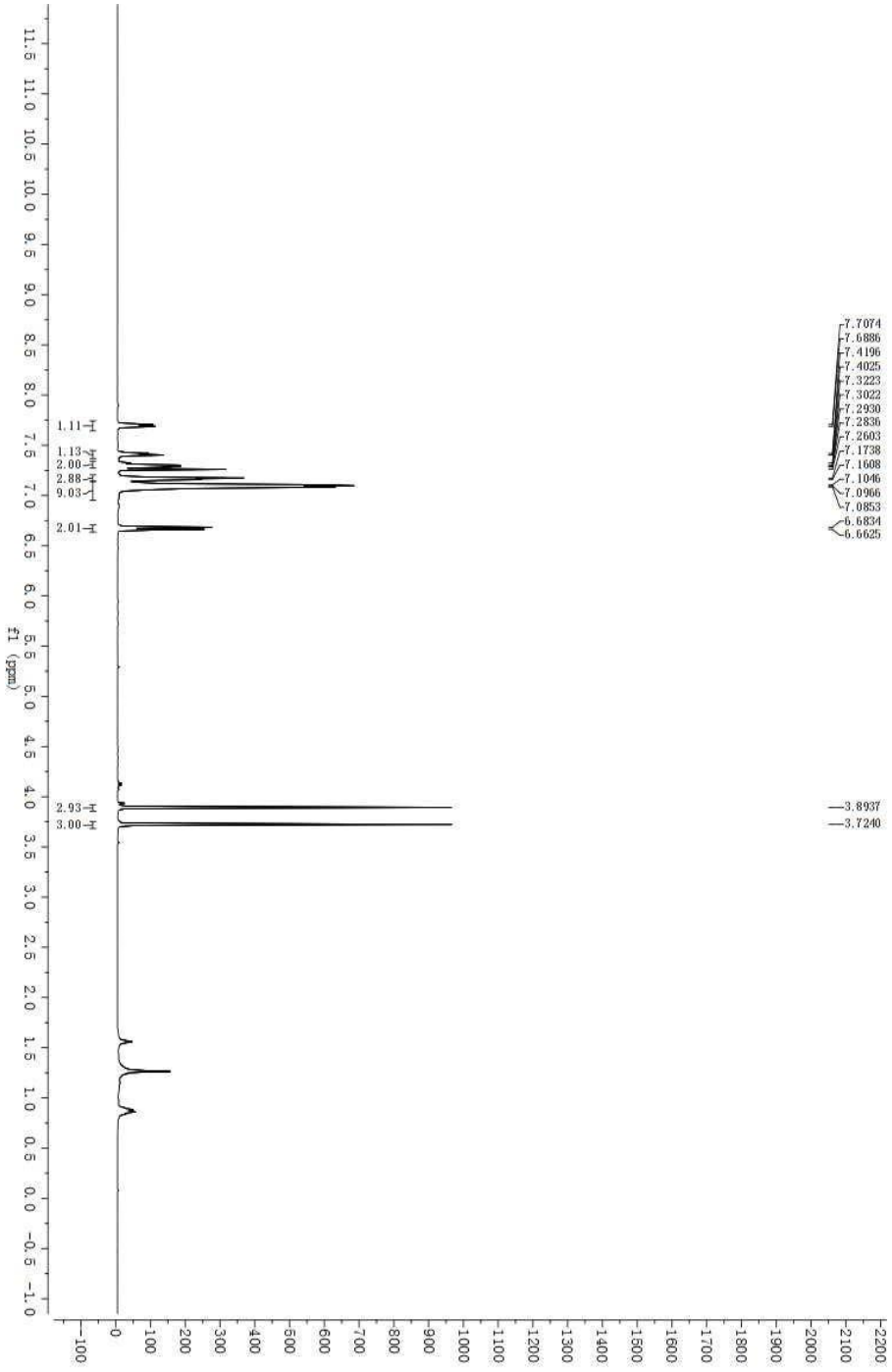

O
OMe
O
I

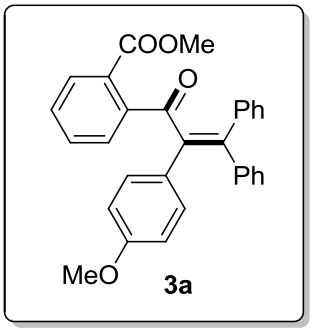
2z


192.88
168.36
154.91
140.07
137.00
131.94
130.81
130.31
129.71
128.78
128.16
128.03
127.89
102.03
77.32
77.00
76.68
52.98
32.97
ppm

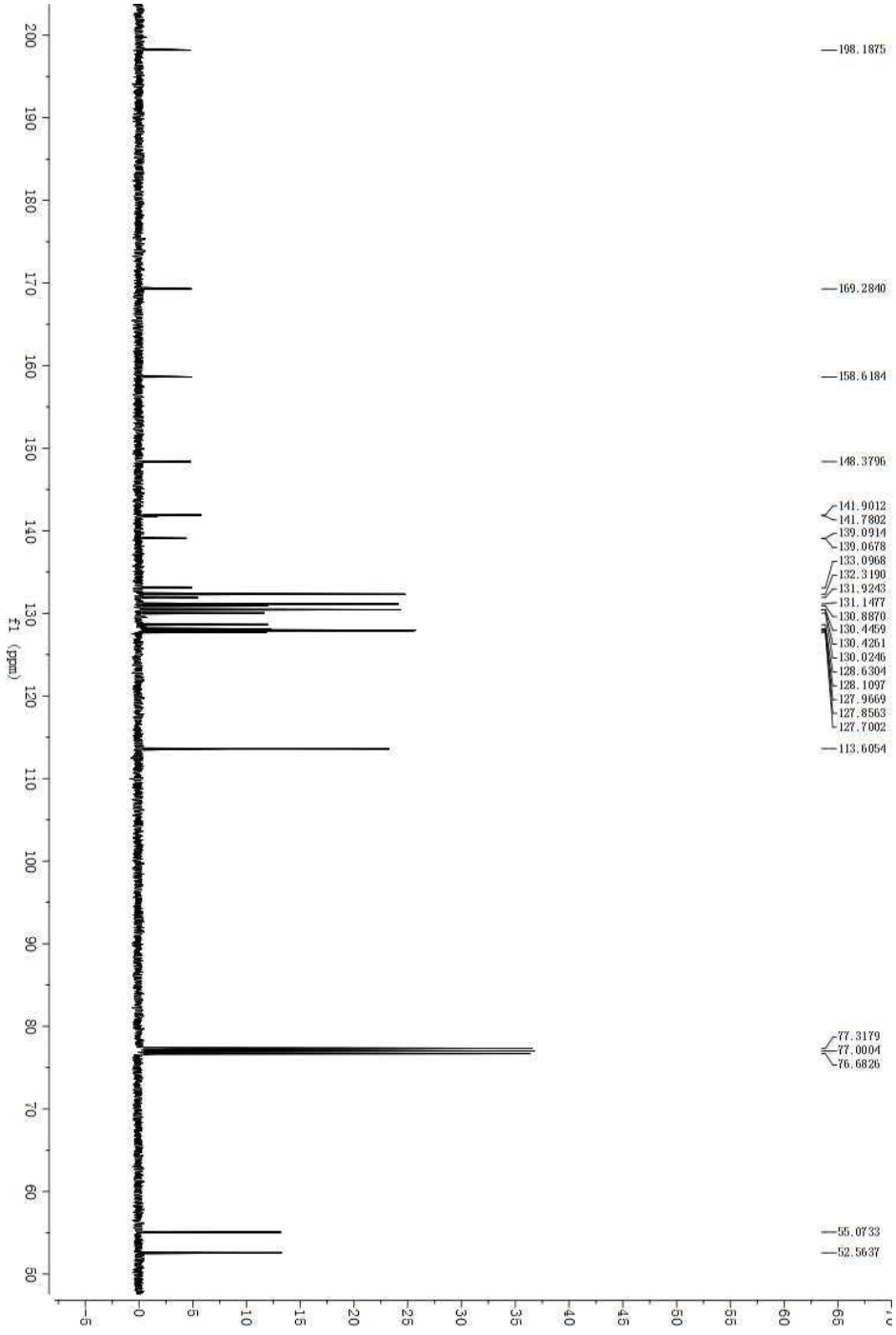

COOMe
O
Ph
Ph
MeO

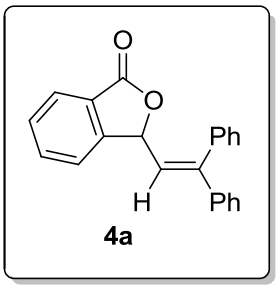
3a


7.7074
7.6886
7.4196
7.4025
7.3223
7.3022
7.2930
7.2836
7.2603
7.1738
7.1608
7.1046
7.0966
7.0853
6.6834
6.6625
3.8937
3.7240
1.11
1.13
2.00
2.88
9.03
2.01
2.93
3.00
f1 (ppm)

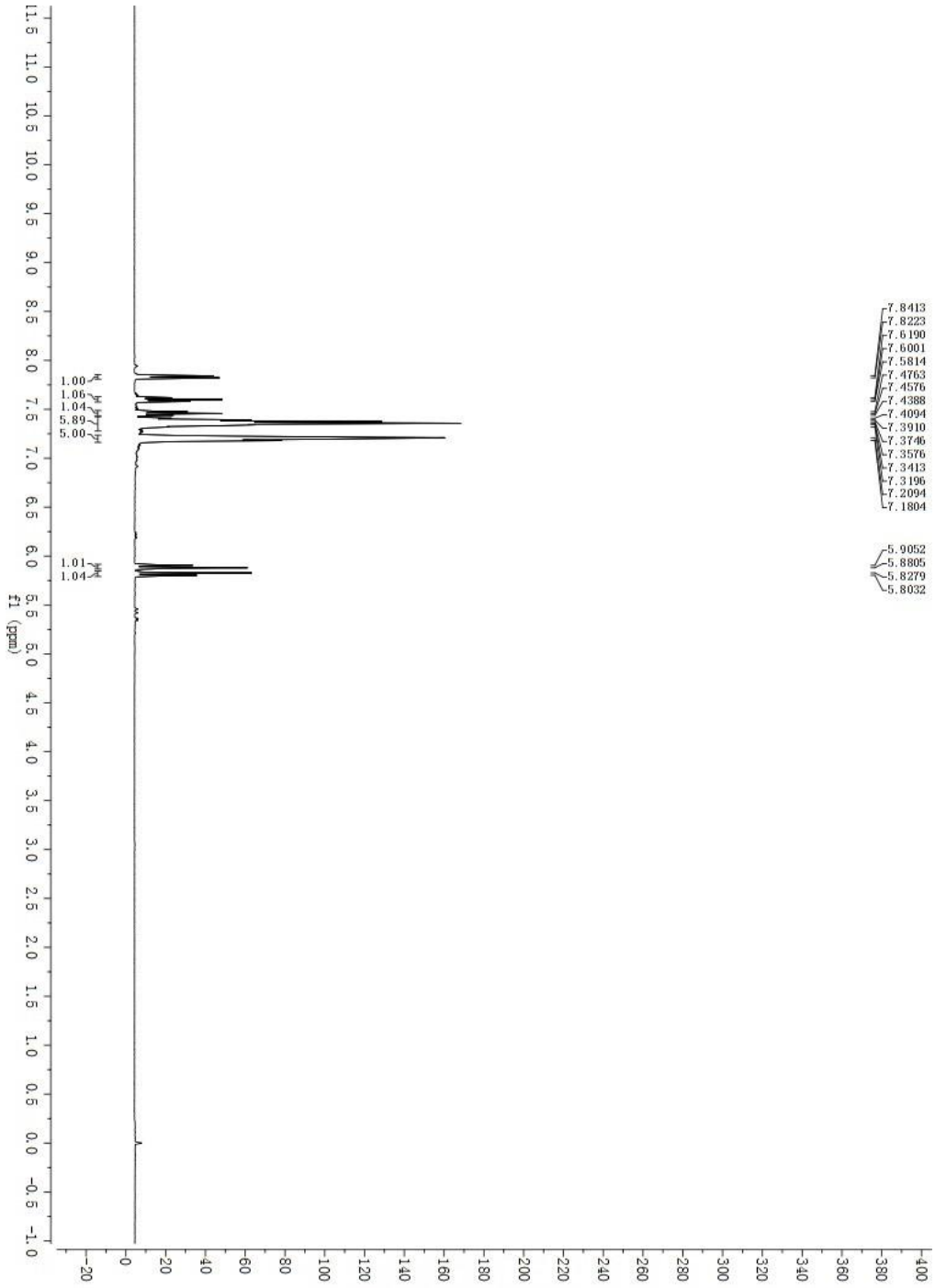

COOMe
O
Ph
Ph
MeO

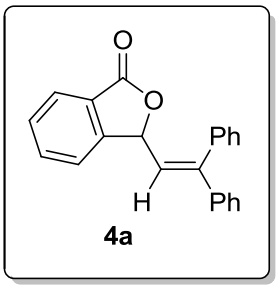
3a


198.1875
169.2840
158.6184
148.3796
141.9012
141.7802
139.0914
139.0678
133.0968
132.3190
131.9243
131.1477
130.8870
130.4459
130.4261
130.0246
128.6304
128.1097
127.9669
127.8563
127.7002
113.6054
77.3179
77.0004
76.6826
55.0733
52.5637
f1 (ppm)

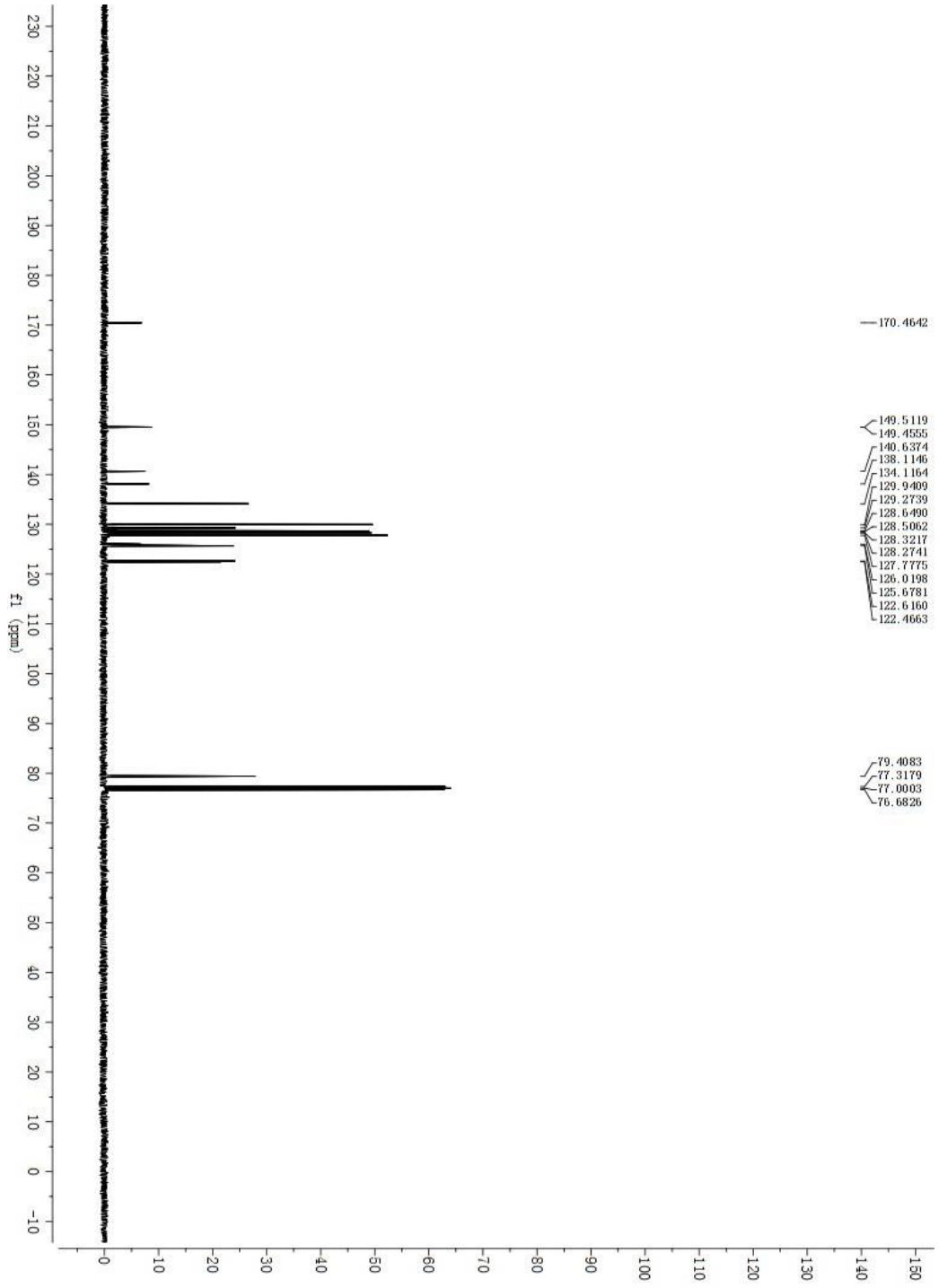

O
O
Ph
H
Ph

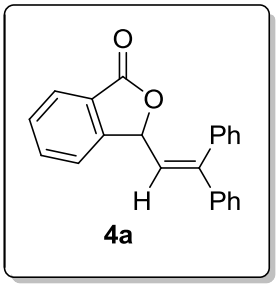
4a


1.00
1.06
1.04
5.89
5.00
1.01
1.04
7.8413
7.8223
7.6190
7.6001
7.5814
7.4763
7.4576
7.4388
7.4094
7.3910
7.3746
7.3576
7.3413
7.3196
7.2094
7.1804
5.9052
5.8805
5.8279
5.8032
f1 (ppm)

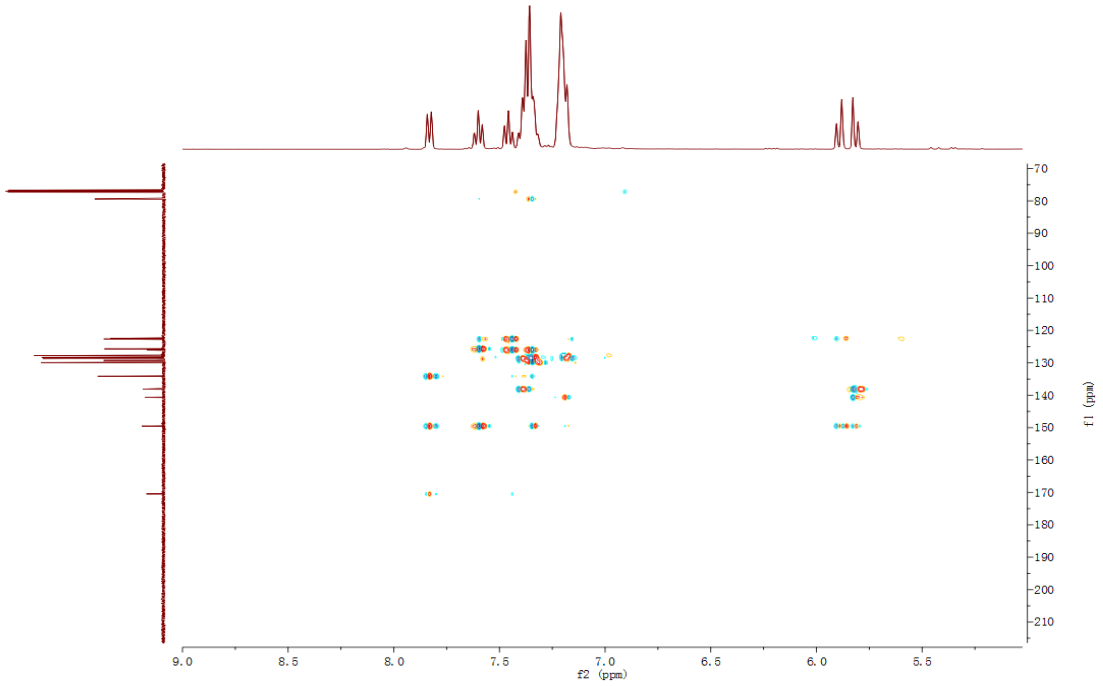

O
O
Ph
H
Ph

4a

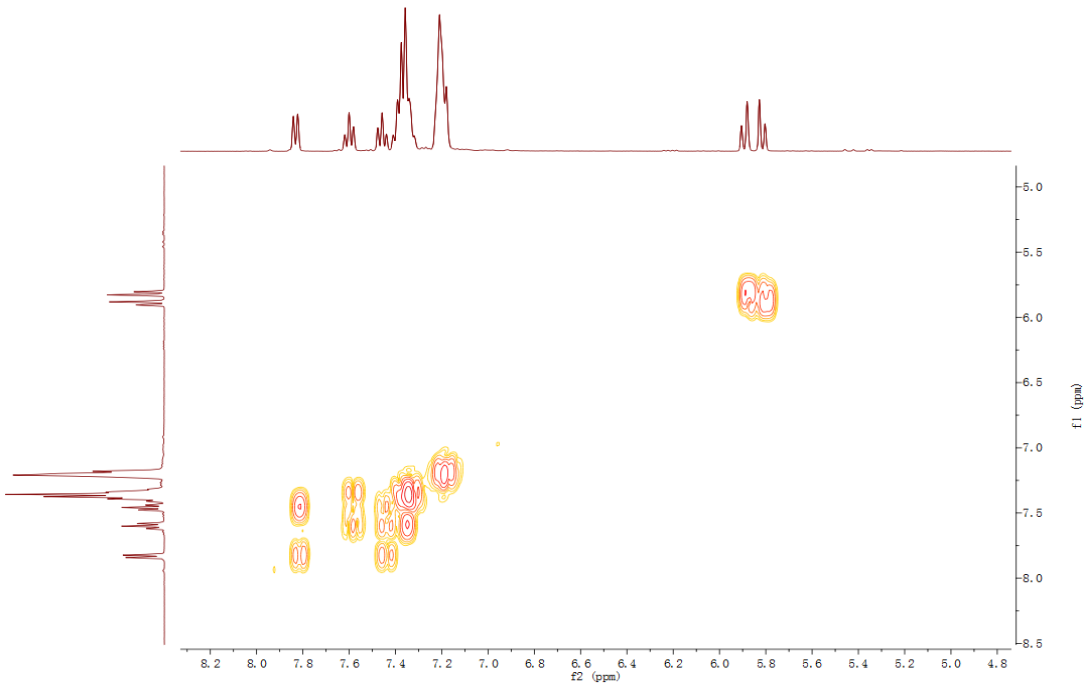

170.4642
149.5119
149.4555
140.6374
138.1146
134.1164
129.9409
129.2739
128.6490
128.5062
128.3217
128.2741
127.7775
126.0198
125.6781
122.6160
122.4663
79.4083
77.3179
77.0003
76.6826
f1 (ppm)

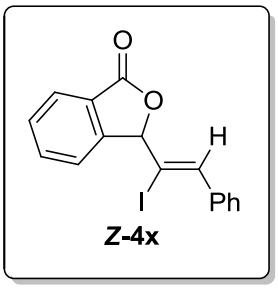


2D-HMBC

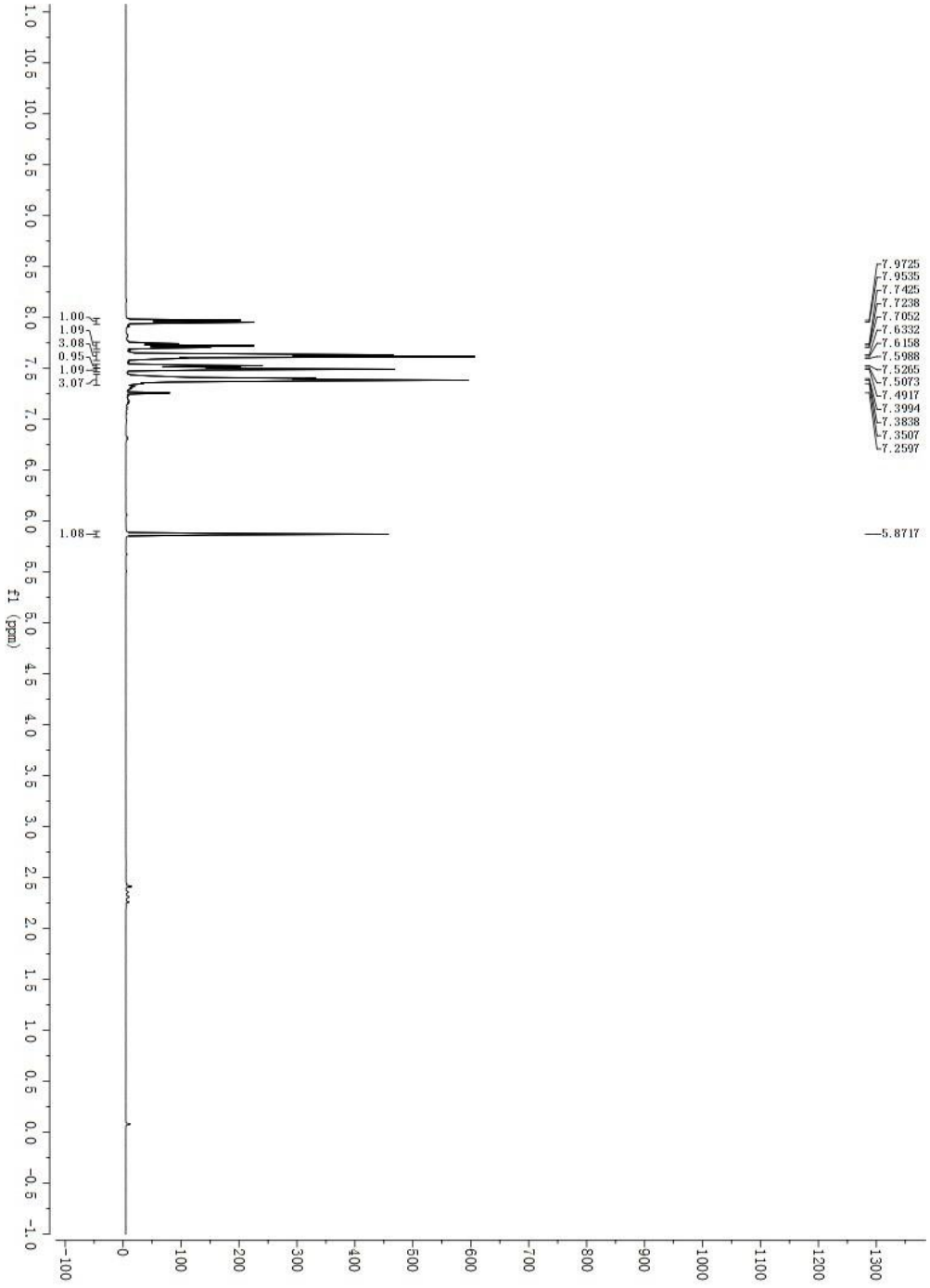


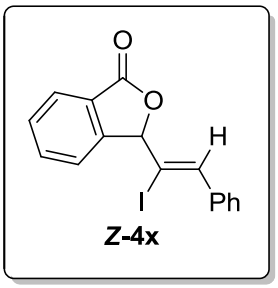
2D-HHCOSY



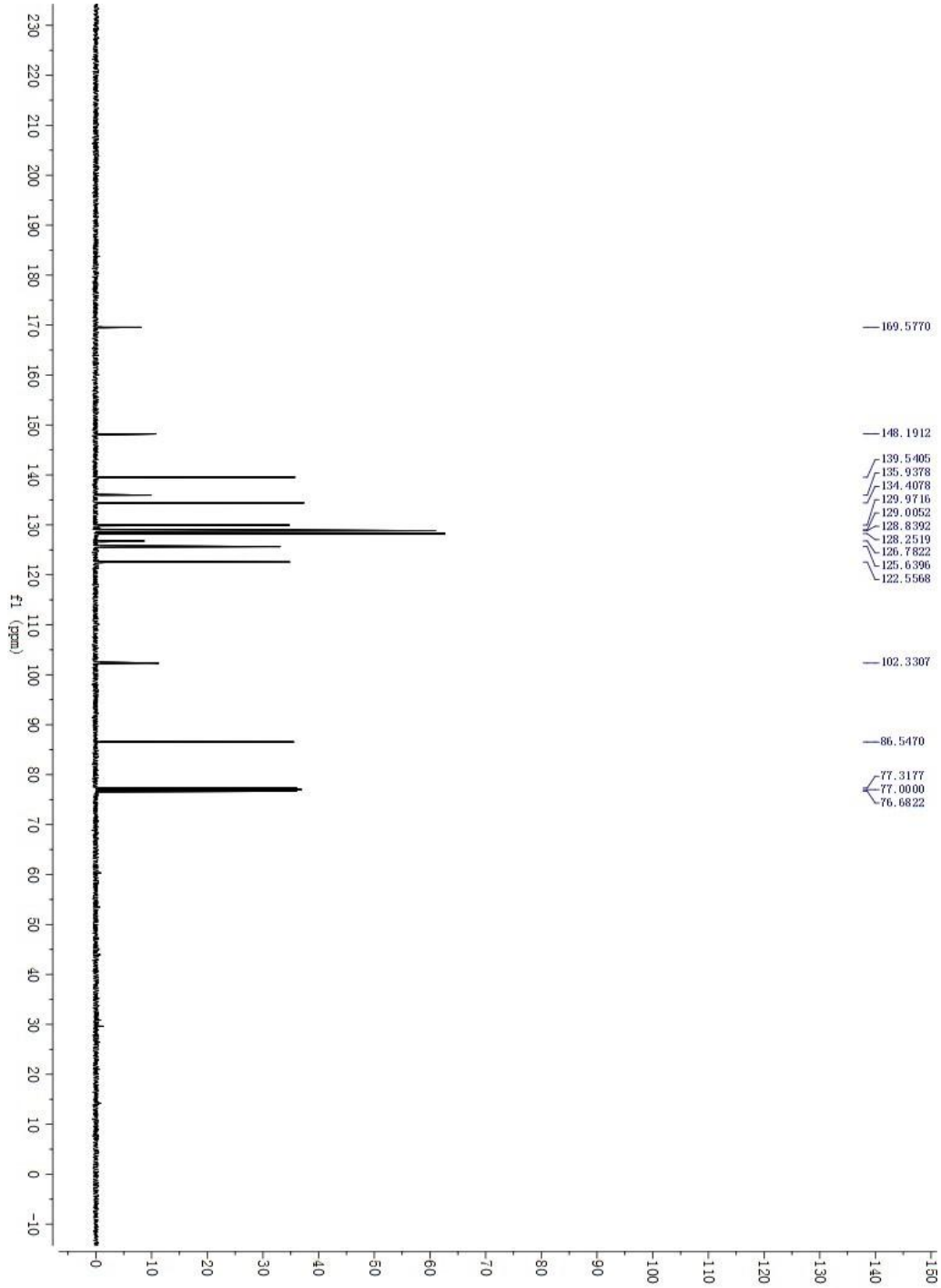

O
O
H
I
Ph

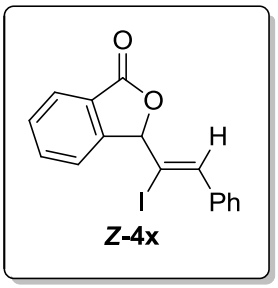
***Z*-4x**


1.00
1.09
3.08
0.95
1.09
3.07
1.08
7.9725
7.9535
7.7425
7.7238
7.7052
7.6332
7.6158
7.5988
7.5265
7.5073
7.4917
7.3994
7.3838
7.3507
7.2597
5.8717
f1 (ppm)


O
O
H
I
Ph

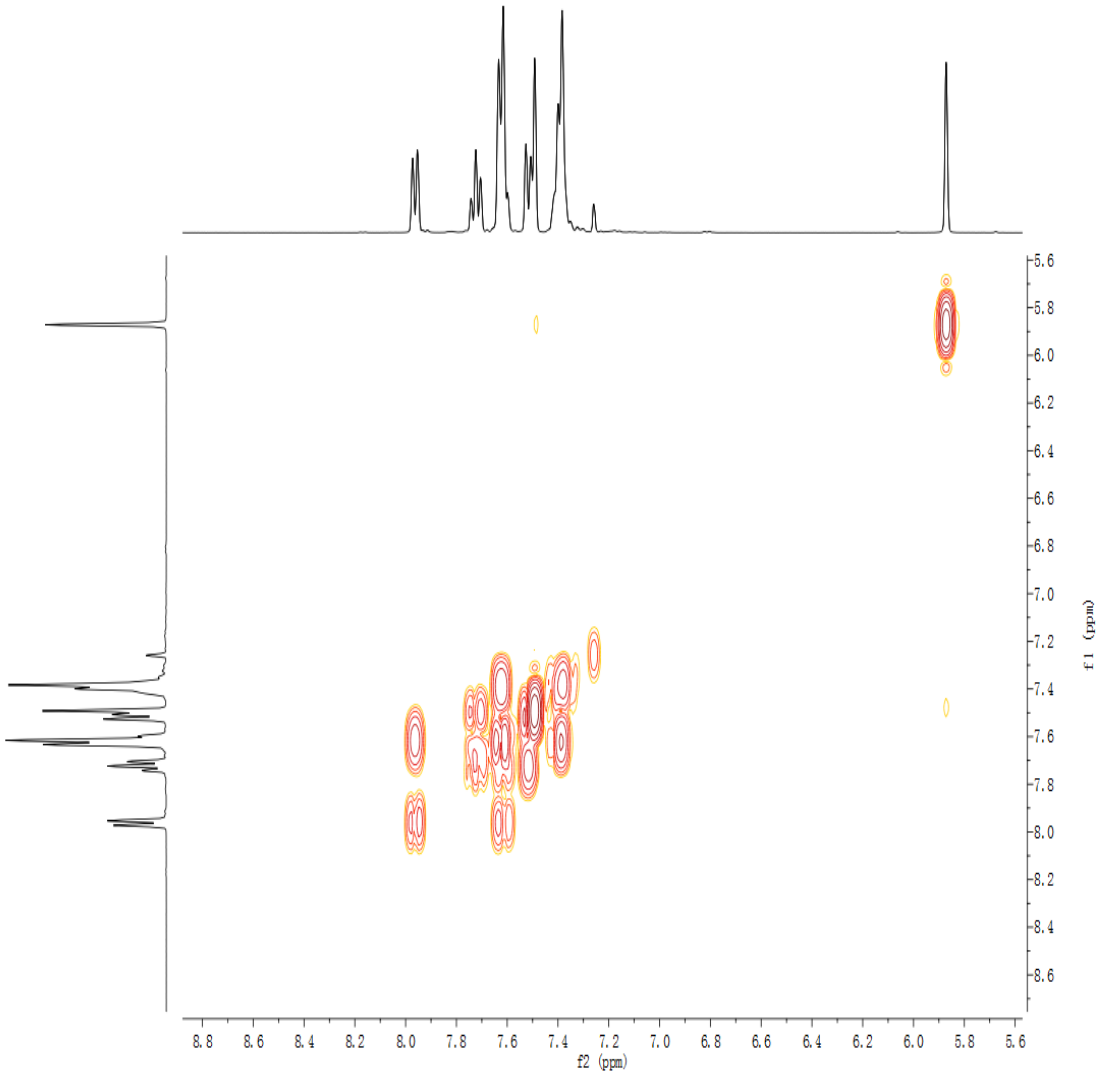
***Z*-4x**

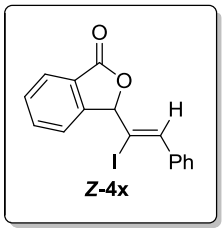

169.5770
148.1912
139.5405
135.9378
134.4078
129.9716
129.0052
128.8392
128.2519
126.7822
125.6396
122.5568
102.3307
86.5470
77.3177
77.0000
76.6822
f1 (ppm)



***Z*-4x**

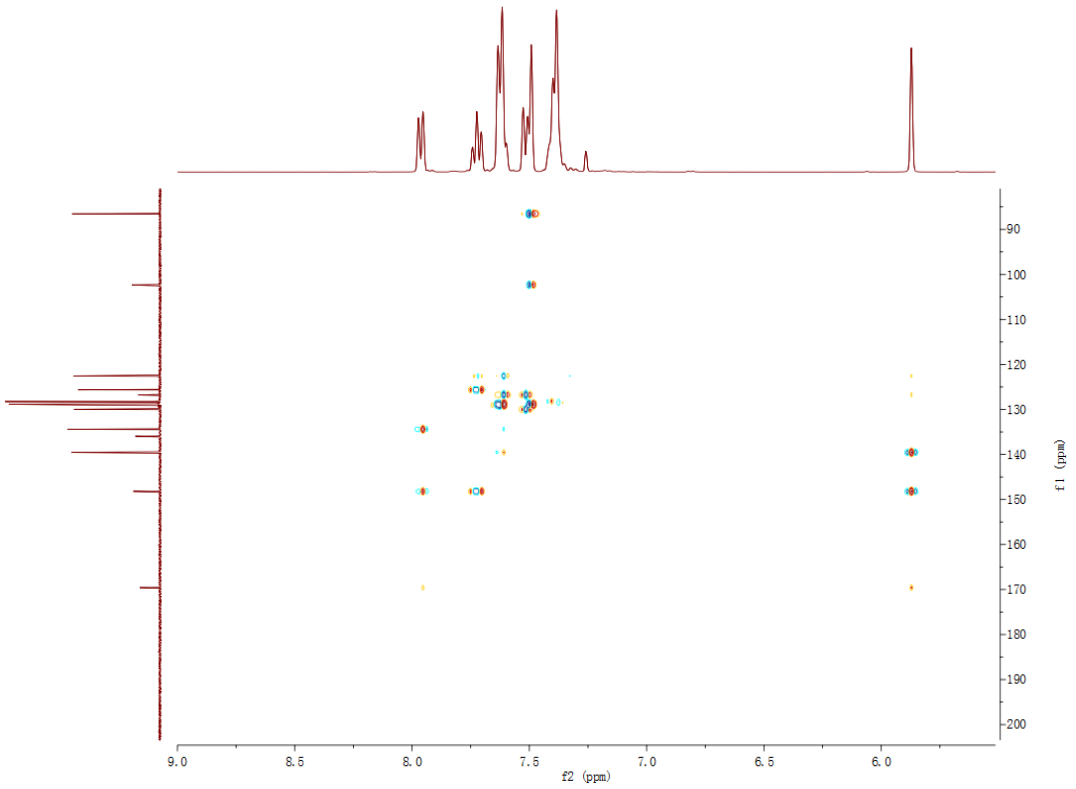
2D-HHCOSY





Z-4x

2D-HMBC



2D-NOESY